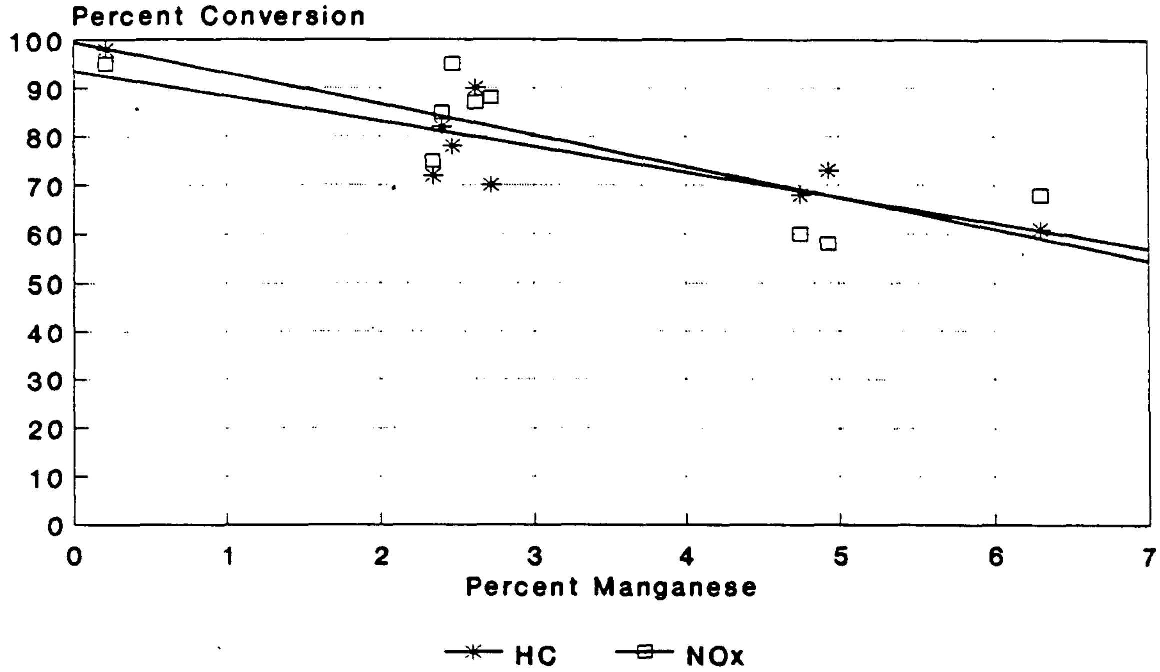

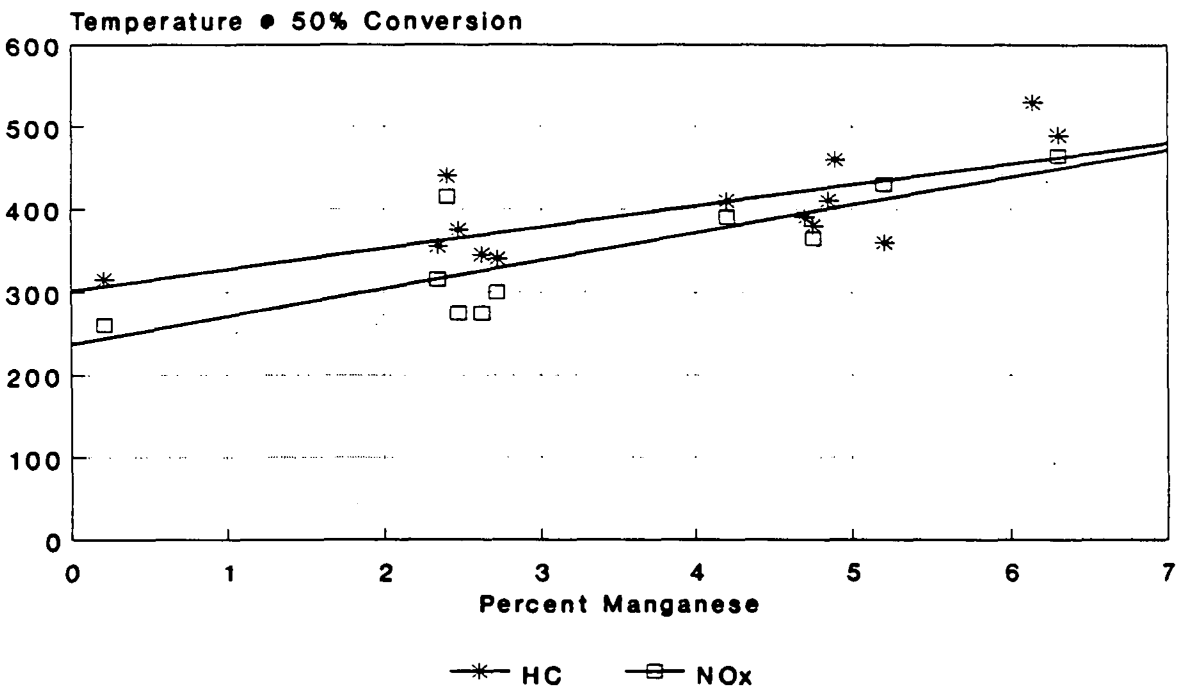

Figure 1

Effect of MMT on Emissions of HC and NOx

In order to determine if a correlation between the source of the catalysts and Mn concentration exists it was necessary to develop a weighting factor. This factor, MMT factor, is:

$$\text{MMT Factor} = (\%\ \text{Mn} / \text{miles}) \times 10000 \times \text{NS}$$

where: miles is in-use miles and
NS is the number of samples from that location.

This factor when plotted (figure 2) against the locations for each sample received shows that the highest MMT factor occurs in Quebec Province with Ontario second. The data includes locations and Mn concentrations from the first series as well as the second series of samples.

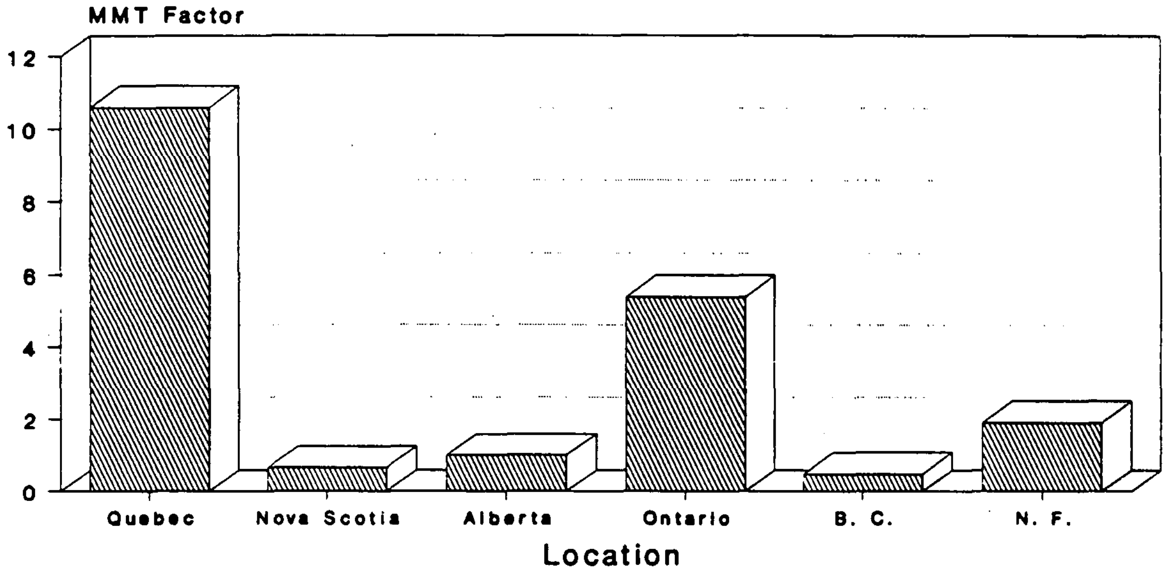

Figure 2

Source of catalyst for series 1 and 2 data

The issue of the effect on catalysts efficiency of contaminants other than Mn_3O_4 was addressed during the SAE presentation using data from the first series. At that time, it was Ethyl's contention that the deteriorating catalyst efficiency was due to Pb, P, and Zn contamination and not Mn_3O_4. Comparisons were shown during the SAE presentation of catalyst activity curves obtained from non-MMT fueled vehicles containing similar amount of Pb, P, and Zn and those vehicles that were fueled with MMT. The data showed that the amounts of Pb, P and Zn encountered in the first series did not have an effect on the catalyst efficiency. Examples of similar comparisons are shown in figures 3 and 4 using samples from series 2 data. This data shows conclusively that the catalysts deterioration is due to the Mn_3O_4 on the surface of the washcoat and not to Pb, P, or Zn.

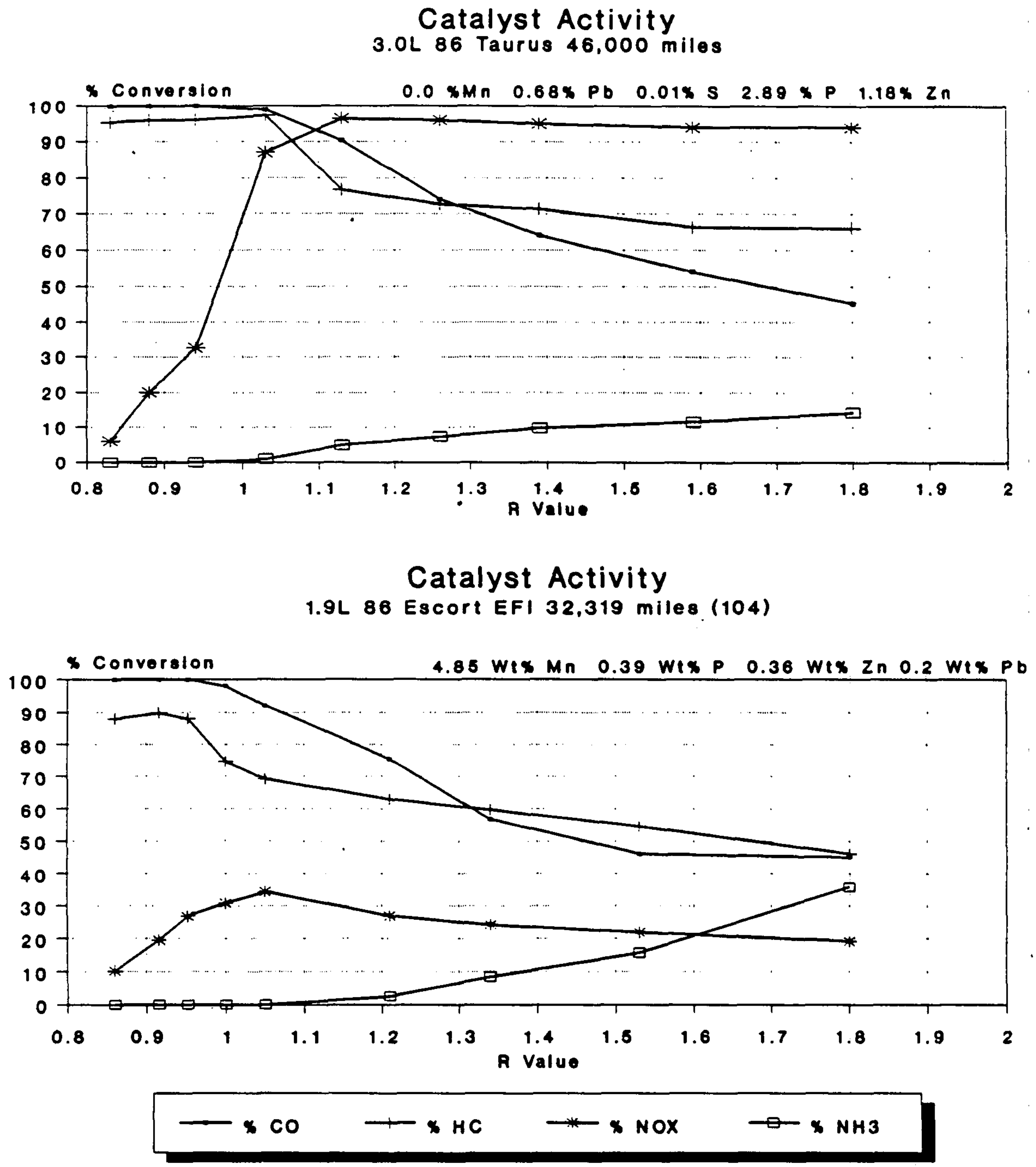

Figure 3

Comparison between Non-MMT Fueled and MMT Fueled Vehicles

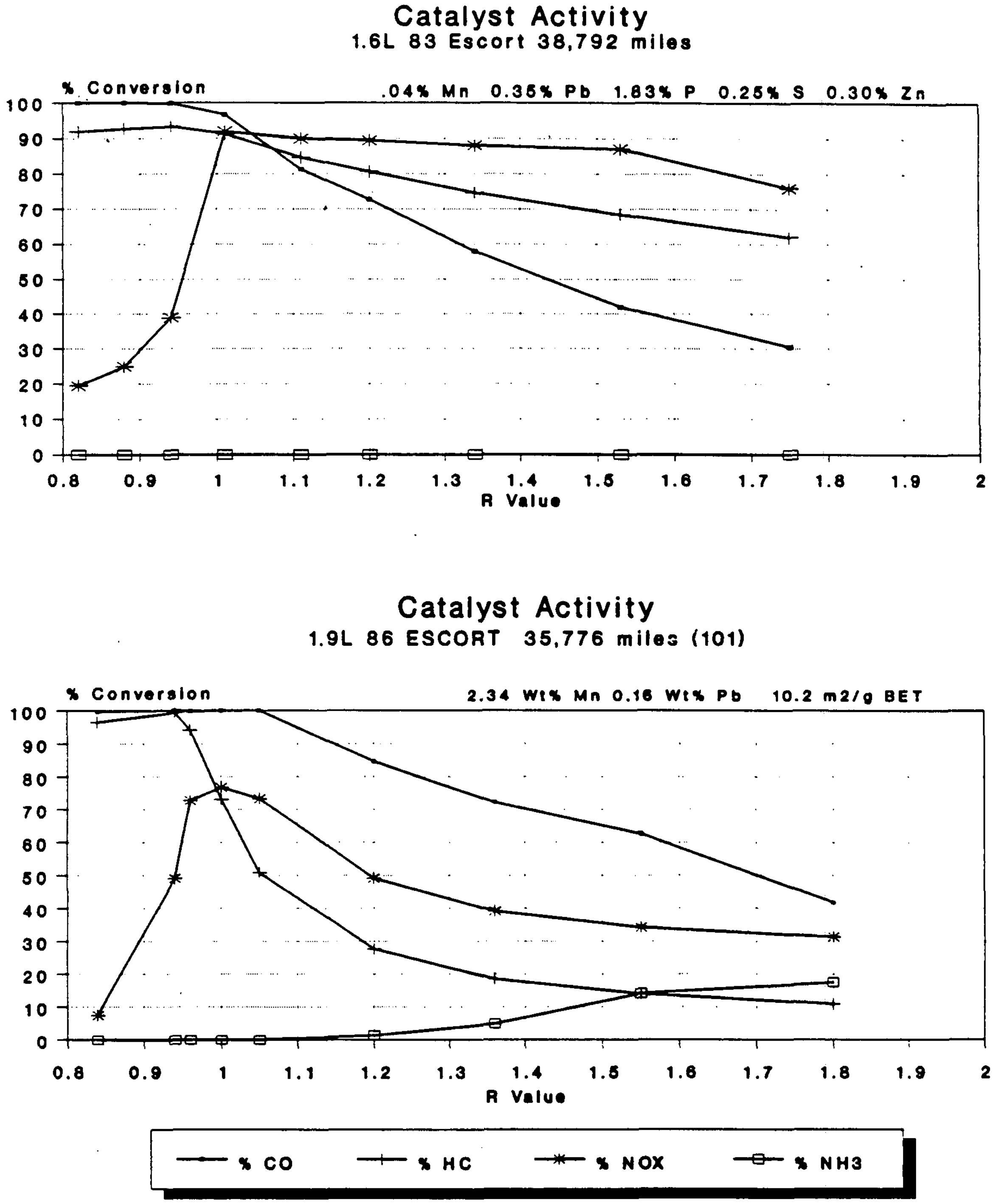

Figure 4

Comparison between Non-MMT Fueled and MMT Fueled Vehicles

Conclusions

In summary, the efficiency of catalyst exposed to the fuel additive MMT is significantly reduced. The data obtained from this series of catalyst confirms those conclusions drawn from the earlier series that MMT does affect the efficiency of the catalyst. The mechanism for failure is the increased mass transfer resistance caused by the layer of Mn_3O_4. Although, the Mn_3O_4 encountered in this series did not appear to be as deleterious,. there was evidence even in the low mileage vehicles that both HC and NO_x efficiency was being reduced. In addition, within the discussion section of this report data on source location and Mn concentration showed that Quebec Province had the highest MMT factor, this correlation is not meant to conclude that the problem of MMT is localized but to determine if a relationship exists. The data appears to point in that direction but no definite conclusion can be drawn because of the limited sample size. In addition, catalyst efficiency comparisons between non-MMT fueled and MMT fueled vehicles show that Pb, P, and Zn in the concentration range observed did not contribute to the deterioration of the catalysts.

The fact that several of the catalysts examined in this second series had signs of being exposed to higher than normal operating temperatures leads one to question the possibility of the effects of Mn_3O_4 on the O_2 sensor. At the mileages encountered experience has shown that it is unlikely that over temperature of the magnitude encountered would have occurred. Hence, there is a possibility that not only the O_2 sensor but other emission components as well are also being affected by the MMT combustion product. For example, if the O_2 sensor was contaminated it would tend to drive the A/F ratio lean, possibly to the point of a lean misfire, and consequently exposing the catalysts to higher than normal temperatures. Since these emission components were not available at the time of analysis no definite conclusion can be reached and this remains an open issue.

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Ignition, Fuel, and Emissions Engineering Department:

R. C. Griffis

References

1. Hurley, R. G., et. al., "Effect of MMT on Catalyst Durability", Letter Report to R. E. Baker, et. al., August 23, 1988.

2. Hurley, R. G., W. L. H. Watkins, and R. C. Griffis, "Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT", SAE 890582, SAE International Congress and Exposition, Detroit, 1989.

TABLE 3
X-Ray Fluorescence and BET Results

TABLE 3

X-RAY FLUORESCENCE ANALYSIS OF CANADIAN CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) COMPONENTS Pt	Rh	Pd	Ce	Ba	Ni	Fe	CONTAMINANTS Pb	S	P	Zn	Mn	Ca	PM Loading g/ft^3	PM Ratio Pt/Pd/Rh
100 2.3L 1984 TEMPO HSC 22,634 MILES																
TWC																
Inlet	xxxx	.10	.020	.002	.82	.47	.83	.42	.06	0	.33	.12	3.13	.03		
Middle	xxxx	.11	.024	.002	.99	.54	1.20	.40	.02	0	.18	.03	1.70	.01	19.3	5/0/1
Outlet	1.2	.11	.024	.001	.88	.51	1.19	.61	.02	0	.19	.08	1.28	.05		
COC																
Inlet	xxxx	.07	.002	.045	.84	.02	.04	.35	.01	0	.08	.02	.81	.01		
Middle	xxxx	.07	.001	.054	.75	.01	.02	.34	0	0	.03	0	.51	.01	19.6	1/1/0
Outlet	xxxx	.08	.001	.080	.81	.02	.03	.34	.01	0	.04	.03	.43	.01		
101 1.9L 1986 ESCORT WAGON 35,776 MILES																
TWC																
Inlet	11.7	.12	.023	.002	.91	.62	1.49	.32	.16	0	.17	.11	2.34	.02		
Middle	10.8	.07	.013	.001	.73	.42	1.18	.27	.05	0	.06	.04	.93	.01	15.9	5/0/1
Outlet	8.2	.08	.015	.002	.78	.46	1.27	.26	.03	0	.08	.04	1.08	.02		
COC																
Inlet	2.7	.08	.001	.057	.67	.01	.01	.33	.19	0	.10	.05	1.98	.02		
Middle	xxxx	.11	0	.087	.93	.01	0	.31	.10	0	.06	.01	.98	.01	25.9	1/1/0
Outlet	2.4	.11	0	.088	.92	.01	0	.32	.09	0	.06	.01	.85	.01		

TABLE 3 (cont.)

X-RAY FLUORESCENCE ANALYSIS OF CANADIAN CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) COMPONENTS Pt	Rh	Pd	Ce	Ba	Ni	Fe	CONTAMINANTS Pb	S	P	Zn	Mn	Ca	PM Loading g/ft^3	PM Ratio Pt/Pd/Rh
102 2.3L 1984 TEMPO HSC 47,149 MILES																
TWC																
Inlet	2.0	.09	.018	.002	.97	.59	1.26	.34	1.60	.05	.34	.36	4.82	.08		
Middle	2.5	.09	.018	.002	1.19	.62	1.65	.32	.34	0	.17	.01	2.54	.05	16.0	5/0/1
Outlet	0.9	.09	.017	.002	1.11	.61	1.55	.31	.20	0	.13	.04	1.83	.02		
COC																
Inlet	0.6	.06	0	.045	.56	.01	.03	.45	1.19	0	.20	.05	2.73	.08		
Middle	0.5	.07	0	.060	.66	.01	.03	.39	.17	0	.09	.01	1.14	.05	16.9	1/1/0
Outlet	0.9	.06	0	.053	.59	0	.03	.37	.14	0	.09	.01	.95	.03		
103 2.8L 1984 BRONCO II 49,467 MILES																
TWC																
Inlet	9.0	.07	.017	.003	.93	.61	1.29	.20	1.30	0	.40	.20	4.89	.01		
Middle	10.1	.06	.017	.002	1.00	.60	1.44	.20	.38	0	.24	.06	3.07	.01	12.0	4/0/1
Outlet	8.6	.06	.018	.002	.93	.59	1.40	.20	.20	0	.18	.04	2.17	.01		
(NOT SURE IF THIS DATA IS 1ST OR 2ND BRICK)																
COC																
Missing																

TABLE 3 (cont.)

X-RAY FLUORESCENCE ANALYSIS OF CANADIAN CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) COMPONENTS Pt	Rh	Pd	Ce	Ba	Ni	Fe	CONTAMINANTS Pb	S	P	Zn	Mn	Ca	PM Loading g/ft^3	PM Ratio Pt/Pd/Rh
104 1.9L 1986 ESCORT EFI 32,319 MILES																
TWC																
Inlet	10.5	.18	.016	0	6.10	.62	.02	.33	.20	.06	.39	.36	4.85	.10		
Middle	18.2	.20	.018	0	6.72	.75	.01	.32	.11	.06	.14	.12	1.16	.02	32.2	12/0/1
Outlet	17.8	.23	.018	0	7.29	.82	.01	.31	.09	.10	.12	.10	.93	.02		
COC																
Inlet	3.4	.07	.001	.056	.76	.01	.01	.24	.16	.51	.33	.12	2.87	.07		
Middle	5.6	.08	.001	.064	.84	.01	.01	.24	.06	.21	.18	.04	1.43	.04	19.6	1/1/0
Outlet	4.7	.07	.001	.061	.78	.01	.01	.23	.04	.17	.16	.03	1.21	.04		
105 1.9L 1986 LYNX 26,971 MILES																
TWC																
Inlet	1.0	.11	.023	.002	1.00	.52	1.26	.22	.01	0	.10	.04	2.40	.02		
Middle	12.1	.11	.020	.002	1.04	.55	1.32	.23	0	0	.06	.02	1.14	.03	18.9	5/0/1
Outlet	13.0	.10	.018	.001	.92	.53	1.23	.22	.03	0	.04	.05	.62	.01		
COC																
Inlet	8.9	.08	0	.060	.55	.01	.01	.28	.50	.05	.10	.07	1.88	.03		
Middle	13.2	.10	0	.081	.68	.01	0	.27	.24	0	.08	.02	1.13	.02	23.5	1/1/0
Outlet	10.4	.09	0	.072	.63	.01	0	.29	.09	0	.08	.02	1.01	.02		

TABLE 3 (cont.)

X-RAY FLUORESCENCE ANALYSIS OF CANADIAN CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) COMPONENTS Pt	Rh	Pd	Ce	Ba	Ni	Fe	CONTAMINANTS Pb	S	P	Zn	Mn	Ca	PM Loading g/ft^3	PM Ratio Pt/Pd/Rh
106 2.5L 1987 TAURUS CFI 39,338 MILES																
TWC																
Inlet	23.3	.10	.021	0	6.38	.73	.81	.28	.02	0	.02	.04	.21	.01		
Middle	21.1	.09	.020	0	6.47	.71	.80	.28	.01	0	.01	.01	.09	.01	17.1	5/0/1
Outlet	21.2	.10	.020	0	5.97	.74	.76	.27	.01	0	0	0	.05	.01		
COC																
Inlet	18.2	.07	0	.059	0	.67	0	.30	.01	0	.01	0	.04	.01		
Middle	22.8	.08	0	.065	0	.73	.01	.29	0	0	0	0	.02	.02	21.9	1/1/0
Outlet	23.9	.08	0	.073	0	.82	0	.28	0	0	0	0	.01	0		
107 2.8L 1985 BRONCO II 27,992 MILES																
TWC																
Inlet	8.3	.13	.025	.003	1.06	.70	1.18	.44	1.39	.11	.24	.10	4.75	.04		
Middle	11.3	.13	.026	.002	1.14	.71	1.29	.41	.12	.01	.12	.03	1.73	.02	23.0	5/0/1
Outlet	9.7	.13	.026	.002	1.02	.71	1.20	.40	.05	.01	.08	.02	1.34	.02		
COC																
Inlet	4.3	.06	0	.044	.59	.01	.01	.25	.21	0	.08	.03	2.25	.02		
Middle	3.2	.08	0	.063	.79	.01	.01	.23	.25	0	.08	.01	.92	.01	19.1	1/1/0
Outlet	6.8	.08	0	.066	.79	.01	.01	.22	.34	0	.06	.01	.73	.01		

TABLE 3 (cont.)

X-RAY FLUORESCENCE ANALYSIS OF CANADIAN CATALYSTS

VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) COMPONENTS							CONTAMINANTS							PM Loading g/ft^3	PM Ratio Pt/Pd/Rh
		Pt	Rh	Pd	Ce	Ba	Ni	Fe	Pb	S	P	Zn	Mn	Ca			
108 2.3L 1985 MUSTANG LX 44,740 MILES																	
TWC																	
Inlet	4.5	.06	.011	.001	.57	.48	.72	.32	.44	0	.63	.31	6.30	.03			
Middle	4.0	.04	.007	.001	.32	.29	.30	.35	.01	0	.18	.05	1.69	.01		8.3	5/0/1
Outlet	3.4	.04	.009	.001	.37	.34	.41	.36	.01	0	.12	.05	1.08	.02			
COC																	
Inlet	1.6	.05	.001	.042	.70	.01	.04	.33	.15	0	.16	.06	1.82	.02			
Middle	0.7	.06	.002	.046	.79	.01	.03	.32	.10	0	.15	.02	1.29	.02		15.3	1/1/0
Outlet	5.6	.06	.001	.052	.80	.01	.02	.33	.21	0	.08	.02	1.00	.03			
109 2.9L 1987 BRONCO II EFI 16,585 MILES																	
TWC																	
Inlet	13.5	.10	.020	0	6.29	.84	0	.30	.15	.14	.13	.07	2.47	.03			
Middle	13.7	.09	.019	0	5.92	.80	0	.32	.07	.07	.04	.03	.56	.02		16.4	5/0/1
Outlet	14.6	.09	.019	0	6.01	.80	0	.30	.05	.08	.04	.02	.50	0			
COC																	
Inlet	24.4	0	.026	.136	3.21	.66	0	.21	.12	.12	.08	.03	1.36	.03			
Middle	20.6	0	.028	.146	3.39	.71	.01	.20	.11	.10	.02	.01	.50	.03		24.3	0/5/1
Outlet	19.7	0	.025	.138	3.23	.68	0	.21	.09	.10	.02	.01	.40	.01			

TABLE 3 (cont.)

X-RAY FLUORESCENCE ANALYSIS OF CANADIAN CATALYSTS

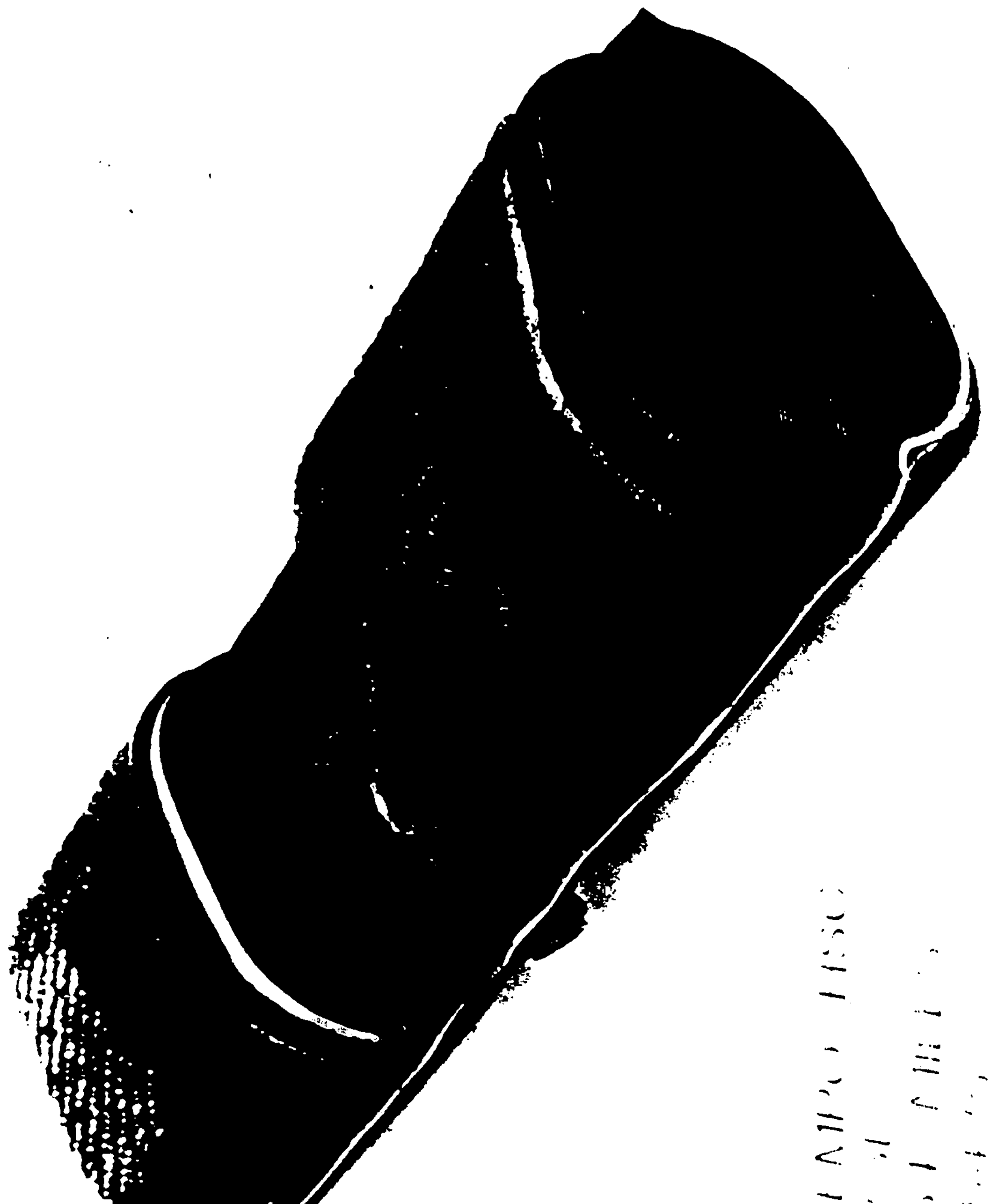
VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) COMPONENTS Pt	Rh	Pd	Ce	Ba	Ni	Fe	CONTAMINANTS Pb	S	P	Zn	Mn	Ca	PM Loading g/ft^3	PM Ratio Pt/Pd/Rh
110 2.8L 1985 RANGER 28,945 MILES																
TWC																
Inlet	2.9	.13	.025	.003	1.02	.64	1.37	.42	.60	.03	.38	.15	4.93	.09		
Middle	1.1	.12	.025	.002	1.04	.58	1.44	.41	.26	0	.20	.05	2.61	.05	21.9	5/0/1
Outlet	1.9	.12	.024	.002	.91	.59	1.27	.41	.22	0	.14	.02	1.72	.03		
COC																
Inlet	xxxx	.06	0	.050	.66	.01	.01	.23	.33	0	.12	.05	2.48	.04		
Middle	xxxx	.07	0	.059	.77	.01	.01	.22	.23	0	.12	.03	1.51	.03	18.2	1/1/0
Outlet	xxxx	.07	0	.064	.78	0	.01	.23	.11	0	.08	.01	1.08	.02		
111 2.9L 1987 BRONCO II EFI 13,545 MILES																
TWC																
Inlet	15.5	.09	.019	0	6.24	.65	0	.32	.02	.16	.09	.05	2.62	.06		
Middle	14.9	.09	.021	0	6.57	.74	0	.32	.01	.05	.02	.02	.68	.02	16.0	5/0/1
Outlet	14.4	.09	.019	0	6.55	.72	0	.34	.01	.02	.07	.01	.83	.02		
COC																
Inlet	21.5	0	.027	.161	3.01	.68	0	.28	.04	.16	.05	.02	1.00	.02		
Middle	22.0	0	.028	.165	3.07	.74	0	.27	.02	.12	.04	.01	.57	.01	27.9	0/6/1
Outlet	17.8	0	.028	.164	3.03	.75	0	.26	.01	.12	.02	0	.44	.01		

TABLE 3 (cont.)

X-RAY FLUORESCENCE ANALYSIS OF CANADIAN CATALYSTS

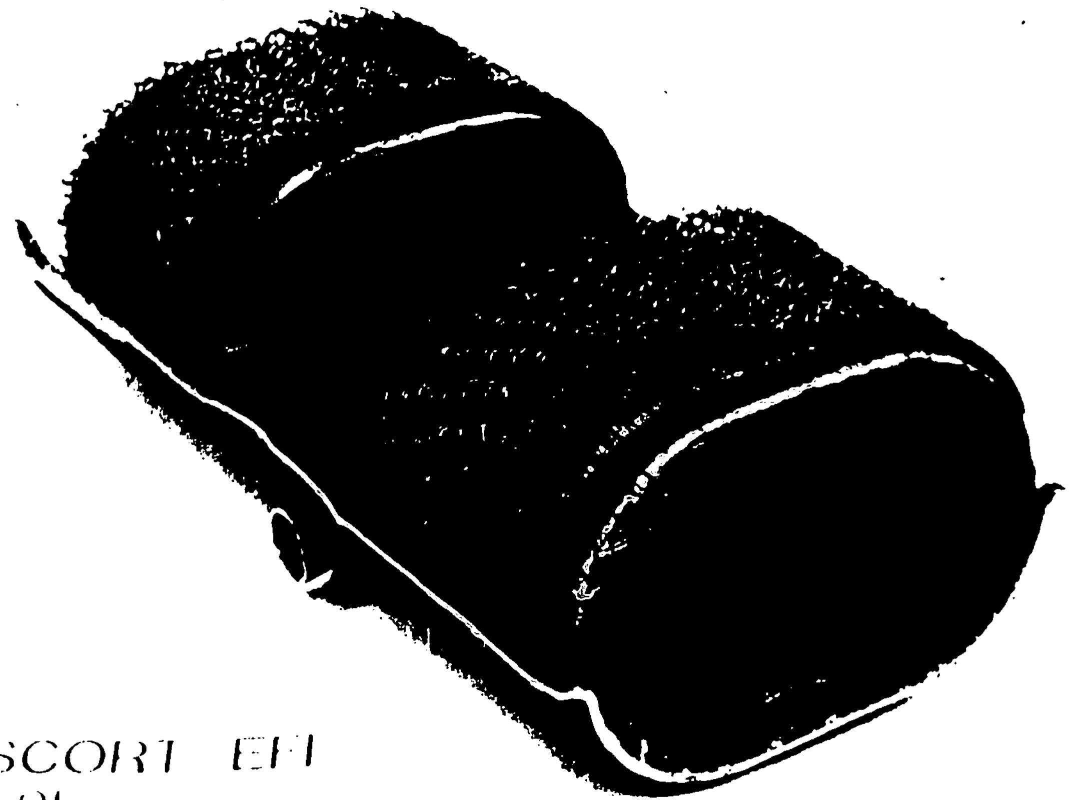
VEHICLE CATALYST	B.E.T. AREA (m^2/g)	XRF Analysis (wt%) COMPONENTS							CONTAMINANTS						PM Loading g/ft^3	PM Ratio Pt/Pd/Rh
		Pt	Rh	Pd	Ce	Ba	Ni	Fe	Pb	S	P	Zn	Mn	Ca		
112 3.03L 1987 AEROSTAR EFI 33,670 MILES																
TWC																
Inlet	15.0	.15	.032	0	5.90	.64	.70	.35	.12	0	.17	.21	2.72	.05		
Middle	13.3	.17	.036	0	6.24	.75	.79	.34	0	0	.09	.02	1.11	.02	29.5	5/0/1
Outlet	17.3	.18	.038	0	6.98	.77	.90	.32	0	0	.06	.01	.89	.02		
COC																
Inlet	16.4	.13	.028	0	6.21	.72	.59	.28	0	0	.11	.03	1.57	.04		
Middle	18.5	.13	.029	0	6.62	.78	.64	.29	0	0	.04	.02	.64	.03	23.7	5/0/1
Outlet	20.6	.14	.031	0	6.90	.79	.69	.26	0	0	.02	.02	.49	.01		

APPENDIX A
As-Received Condition of Catalysts

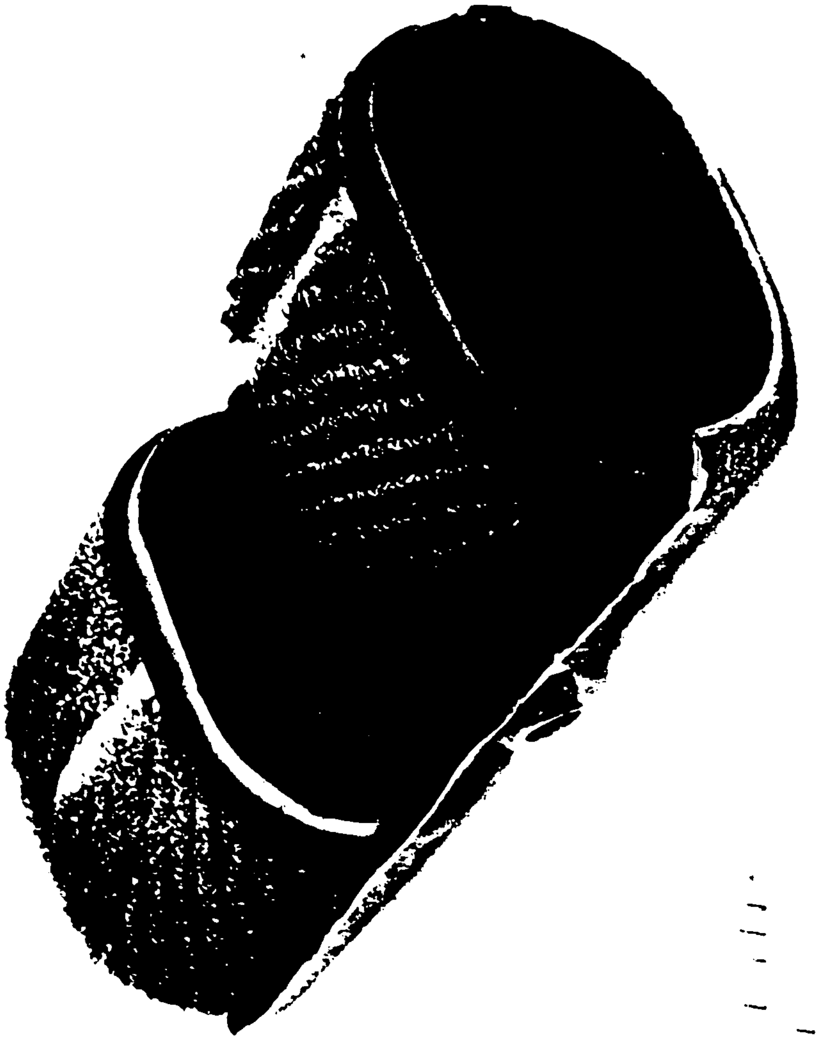


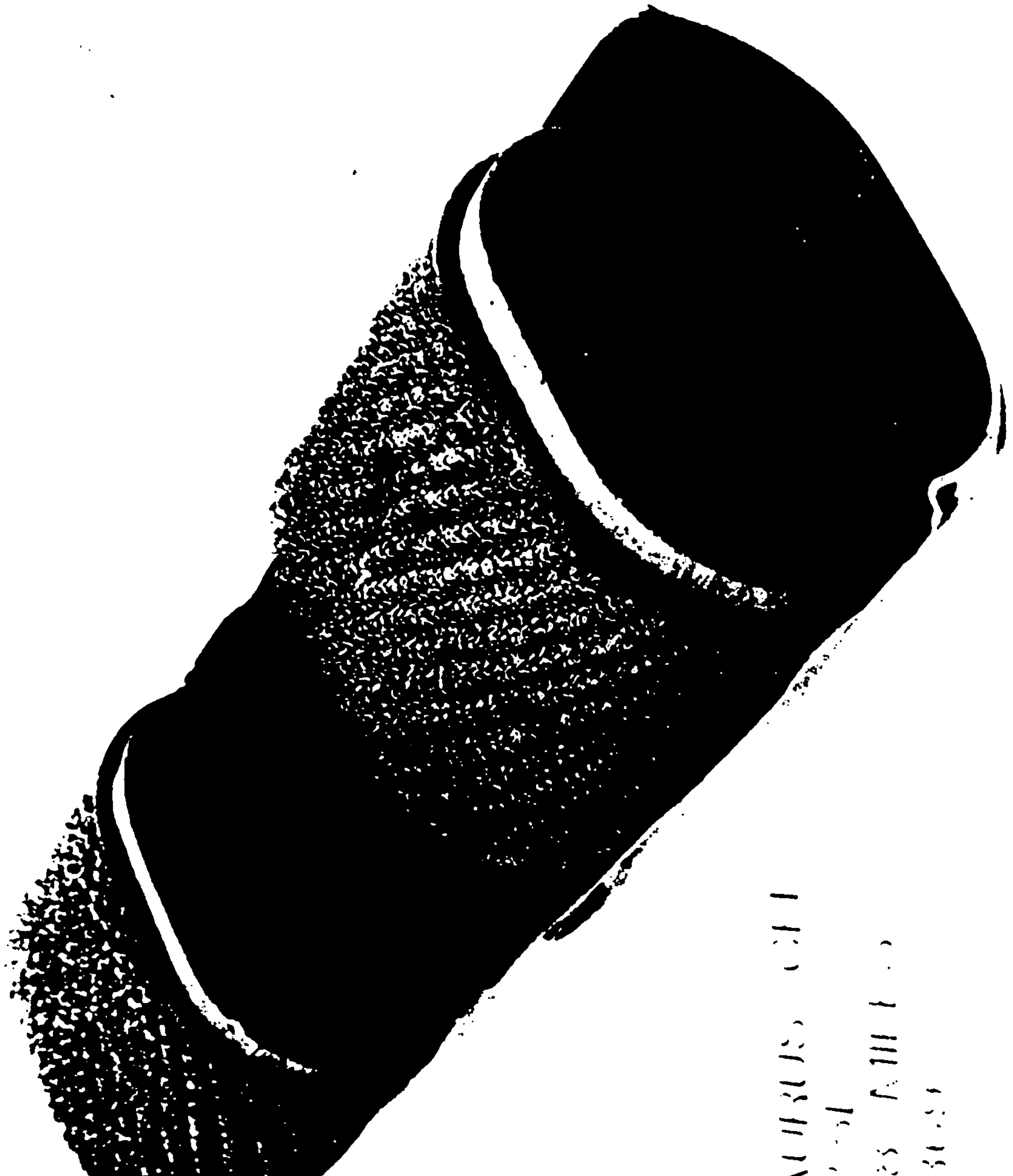

ESCORT
MILES

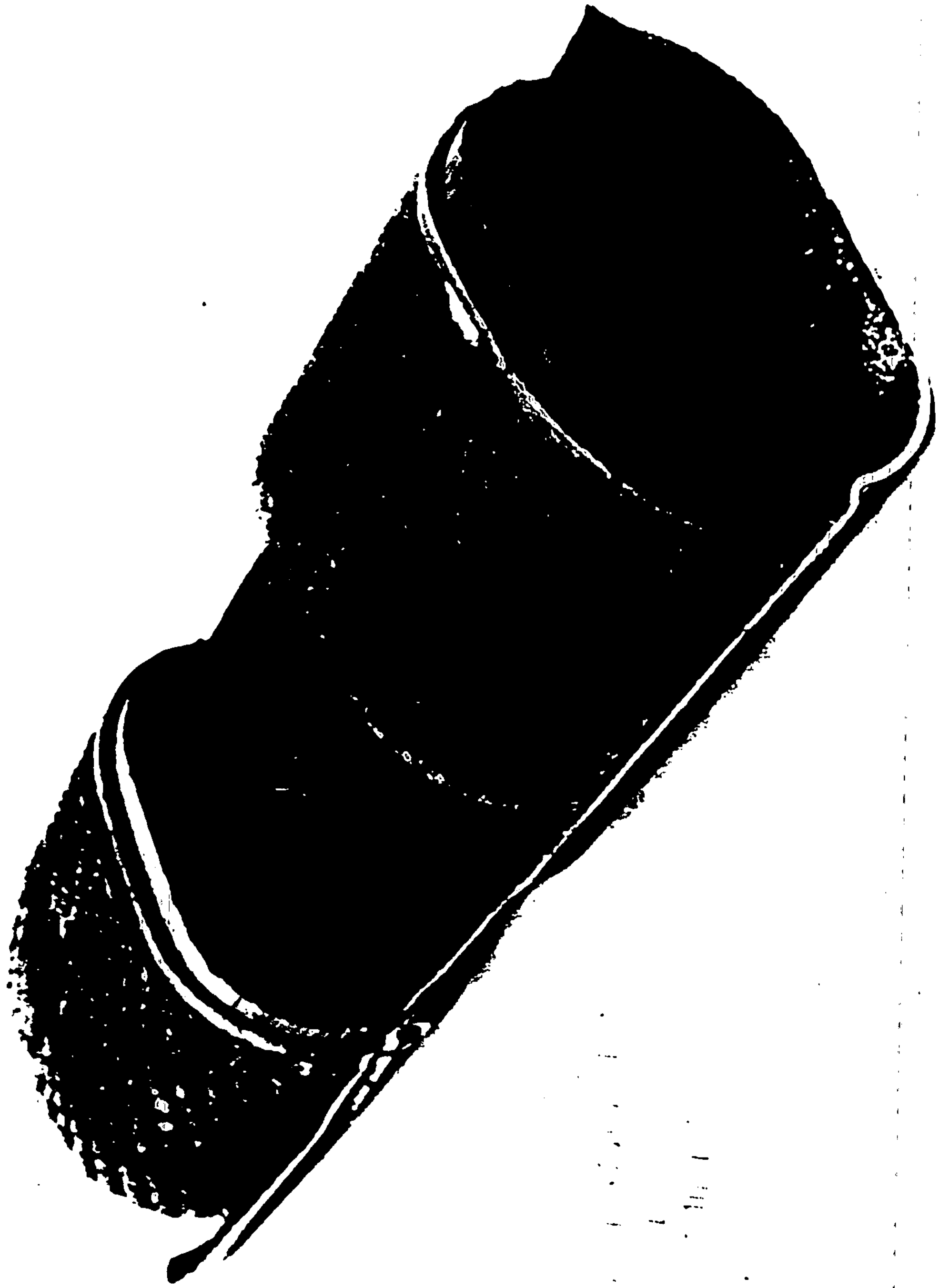
1984 BRONCO II
2.8L
49,467 MILES
010961

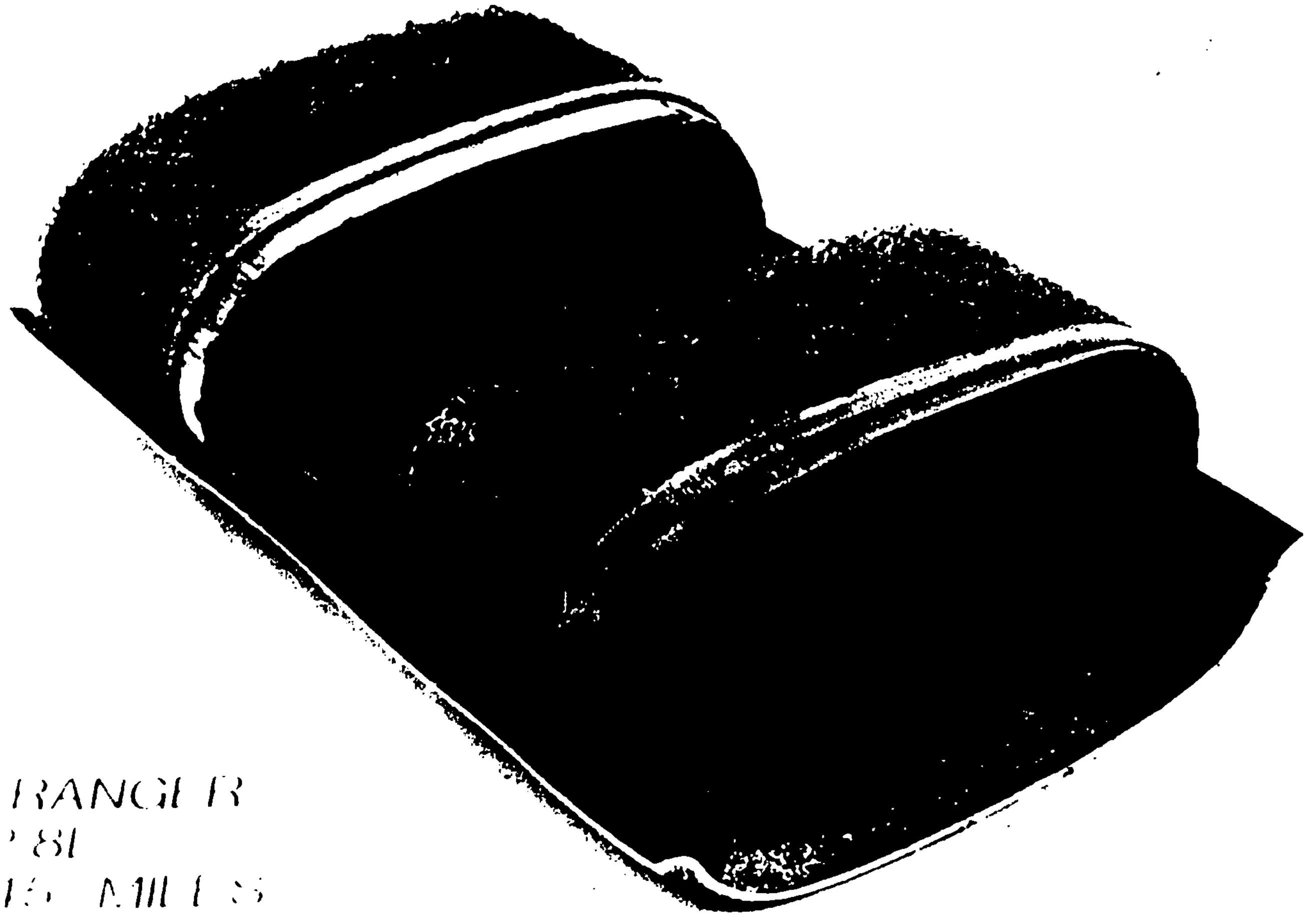


1986 ESCORT EFI
1.9L
32,319 MILES
178409









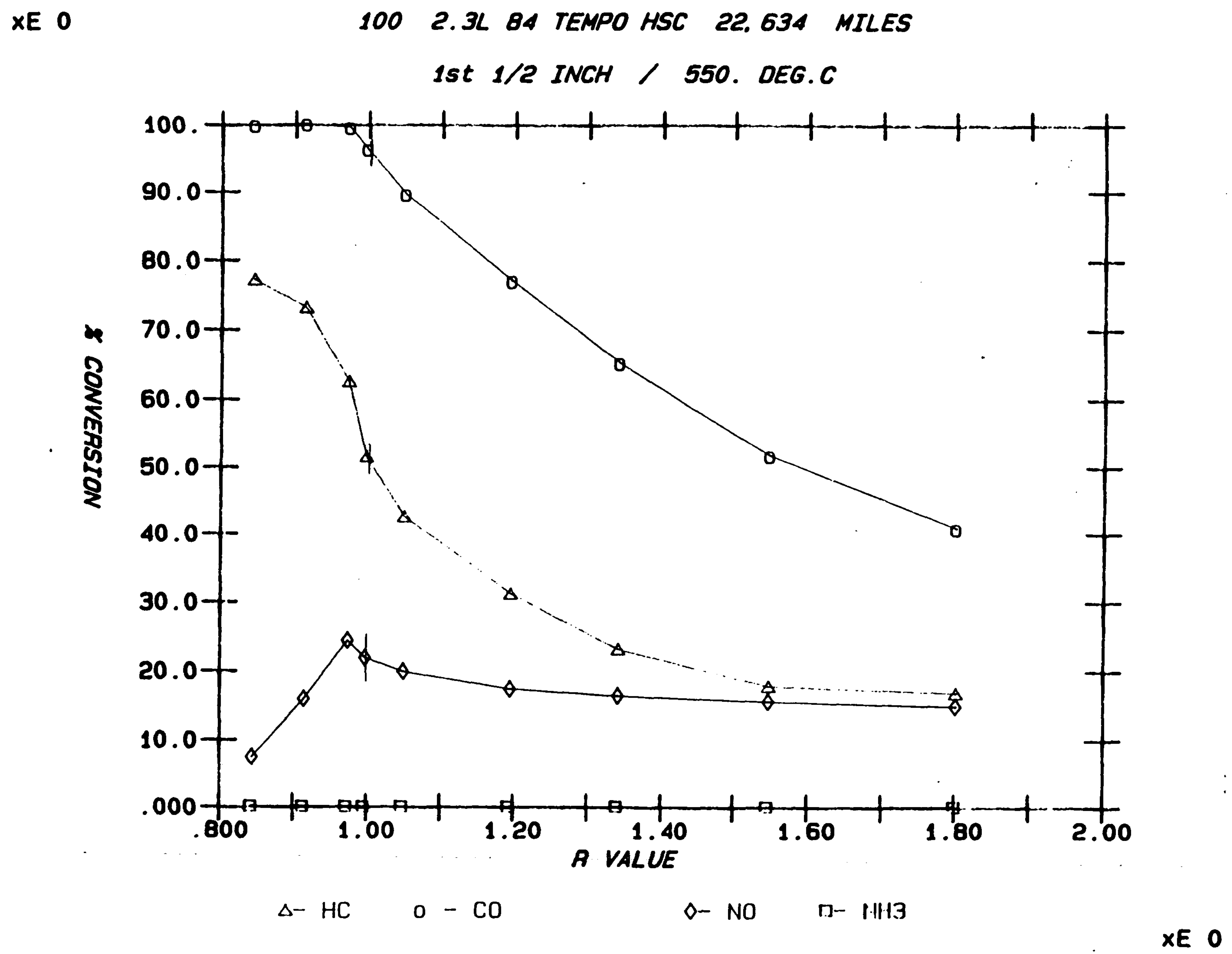
1985 RANGER
2.8L
[illegible] MILES
[illegible]


1987 BRONCO II EFI
2.9l
13.545 MILES
015516

133

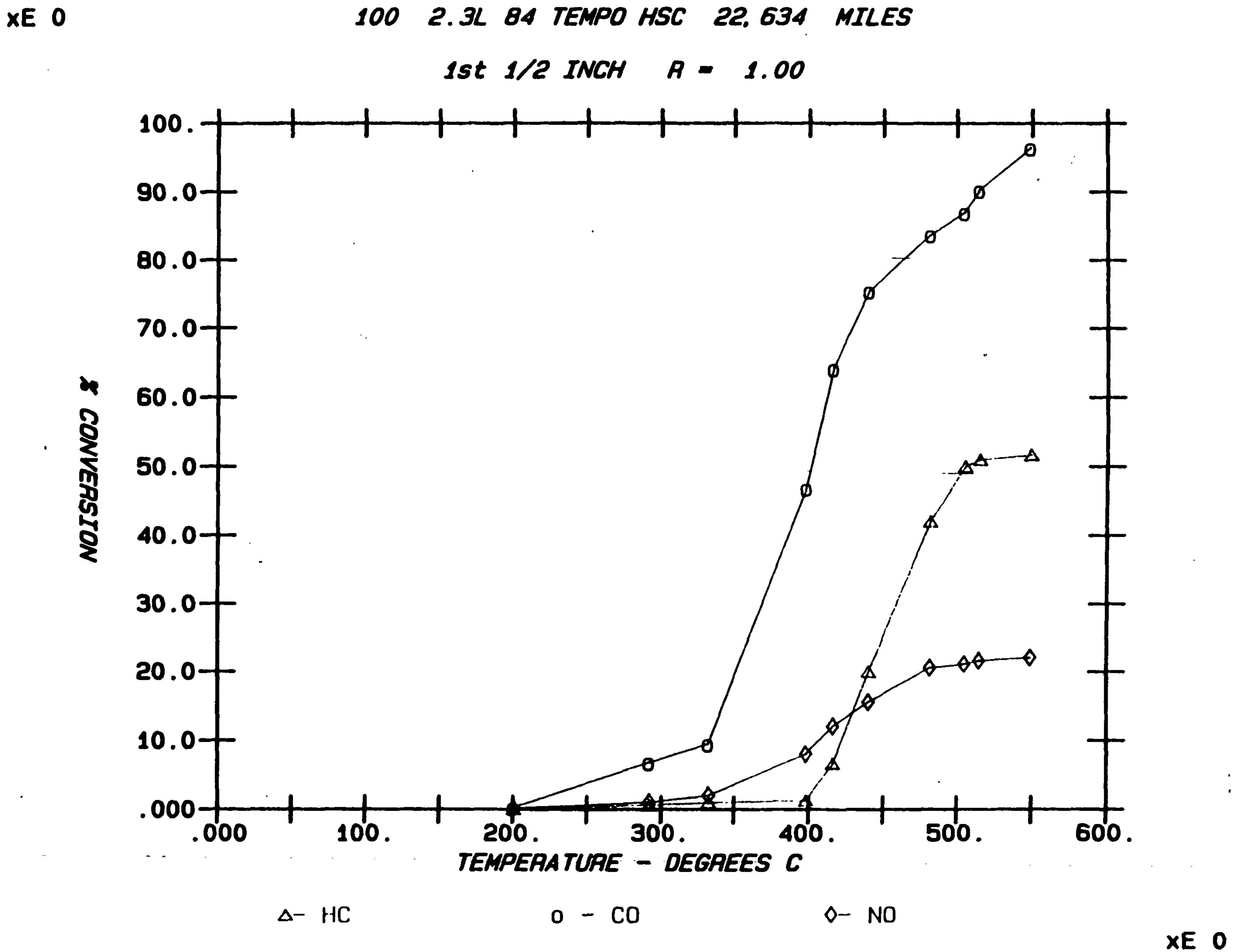
1987 AERO STAR
3.0L
33,670 MILES
052327

APPENDIX B
Catalysts Efficiency and Light-Off Curves



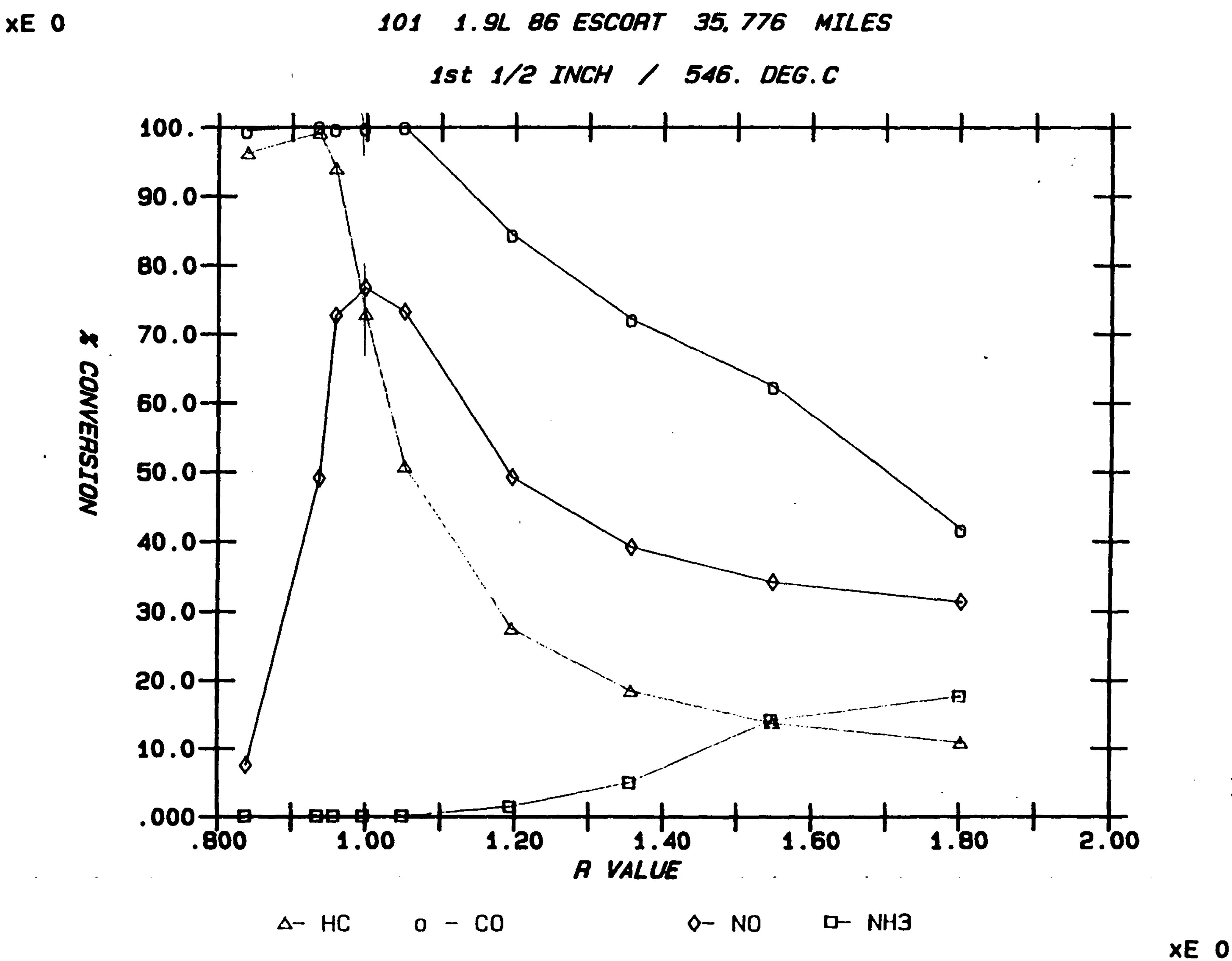
xE 0
100 2.3L 84 TEMPO HSC 22,634 MILES
1st 1/2 INCH / 550. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
Δ– HC
o – CO
◇– NO
□– NH3
xE 0

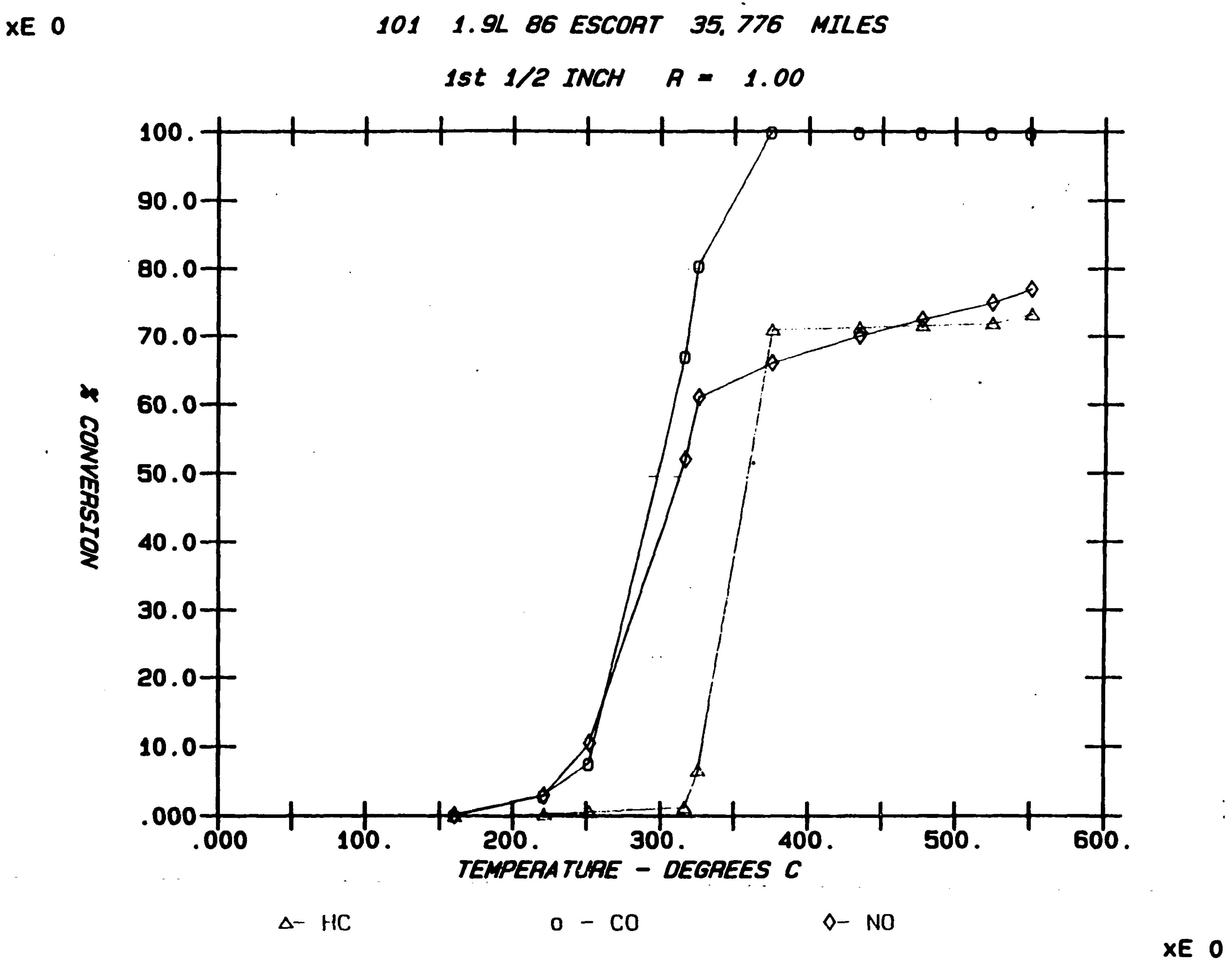
135



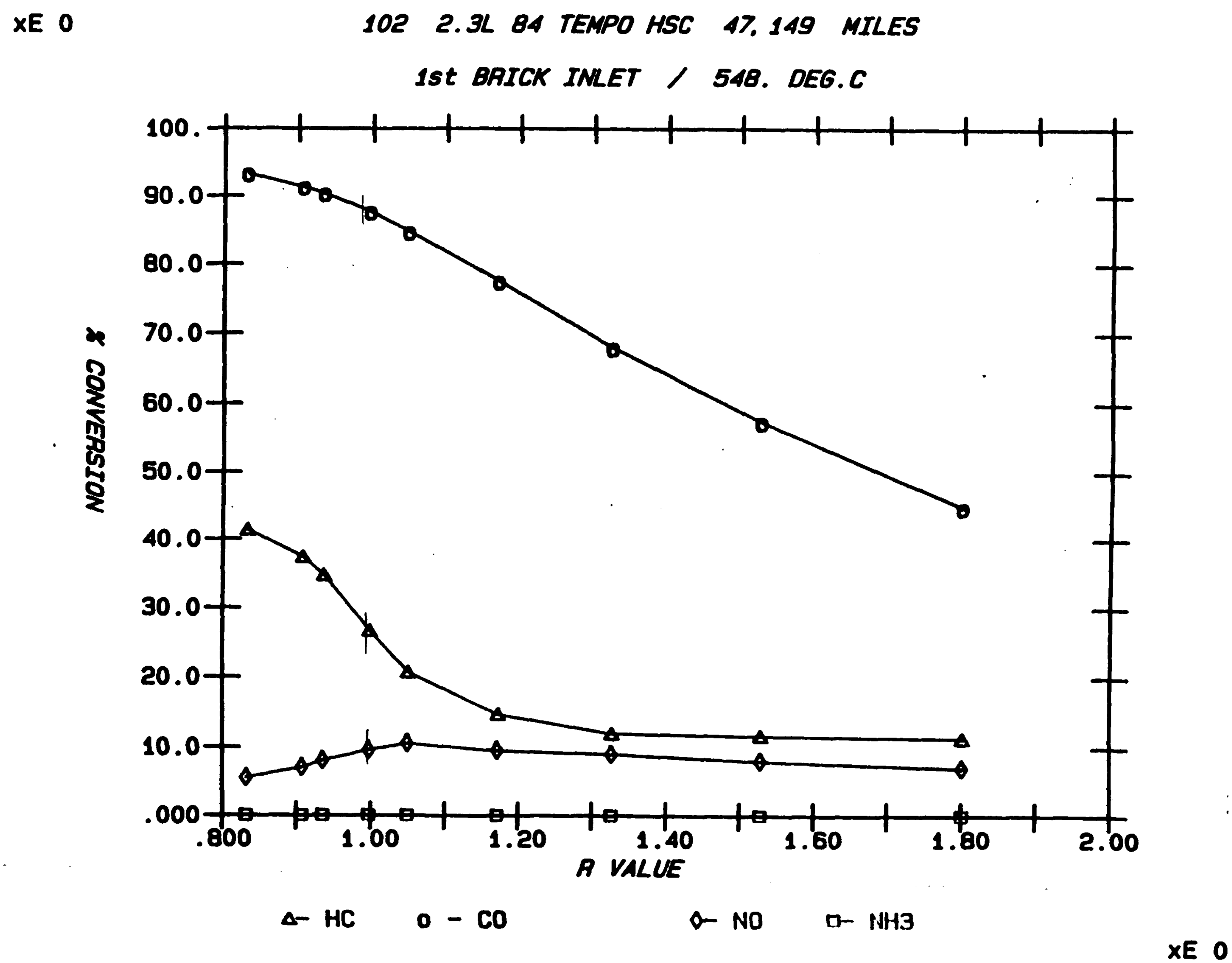
xE 0
100 2.3L 84 TEMPO HSC 22,634 MILES
1st 1/2 INCH R = 1.00
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
△- HC
o - CO
◇- NO
xE 0

136

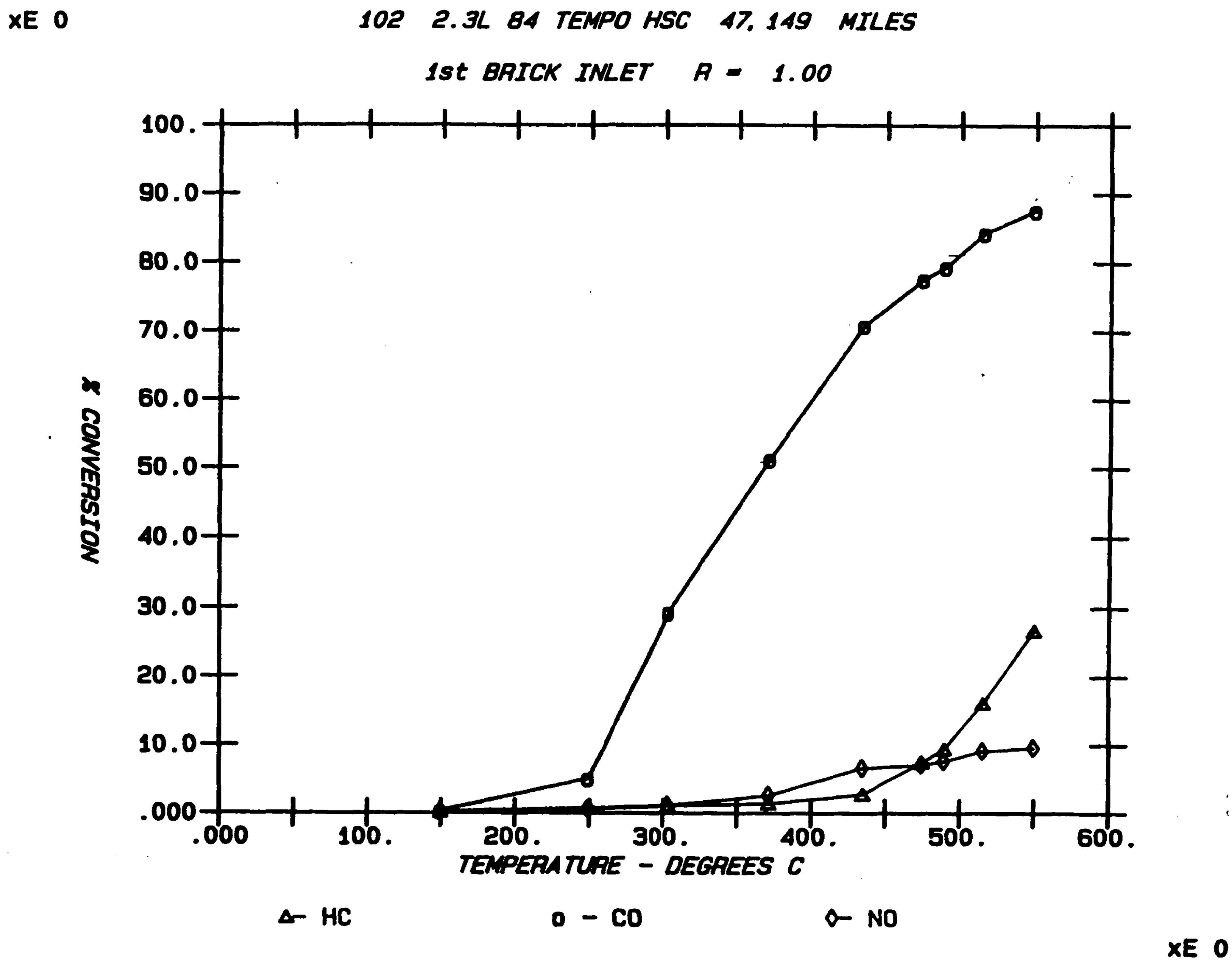

xE 0
101 1.9L 86 ESCORT 35,776 MILES
1st 1/2 INCH / 546. DEG.C
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
△– HC
o – CO
◇– NO
□– NH3
xE 0


xE 0
101 1.9L 86 ESCORT 35,776 MILES
1st 1/2 INCH R = 1.00
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
△- HC
o - CO
◇- NO
xE 0

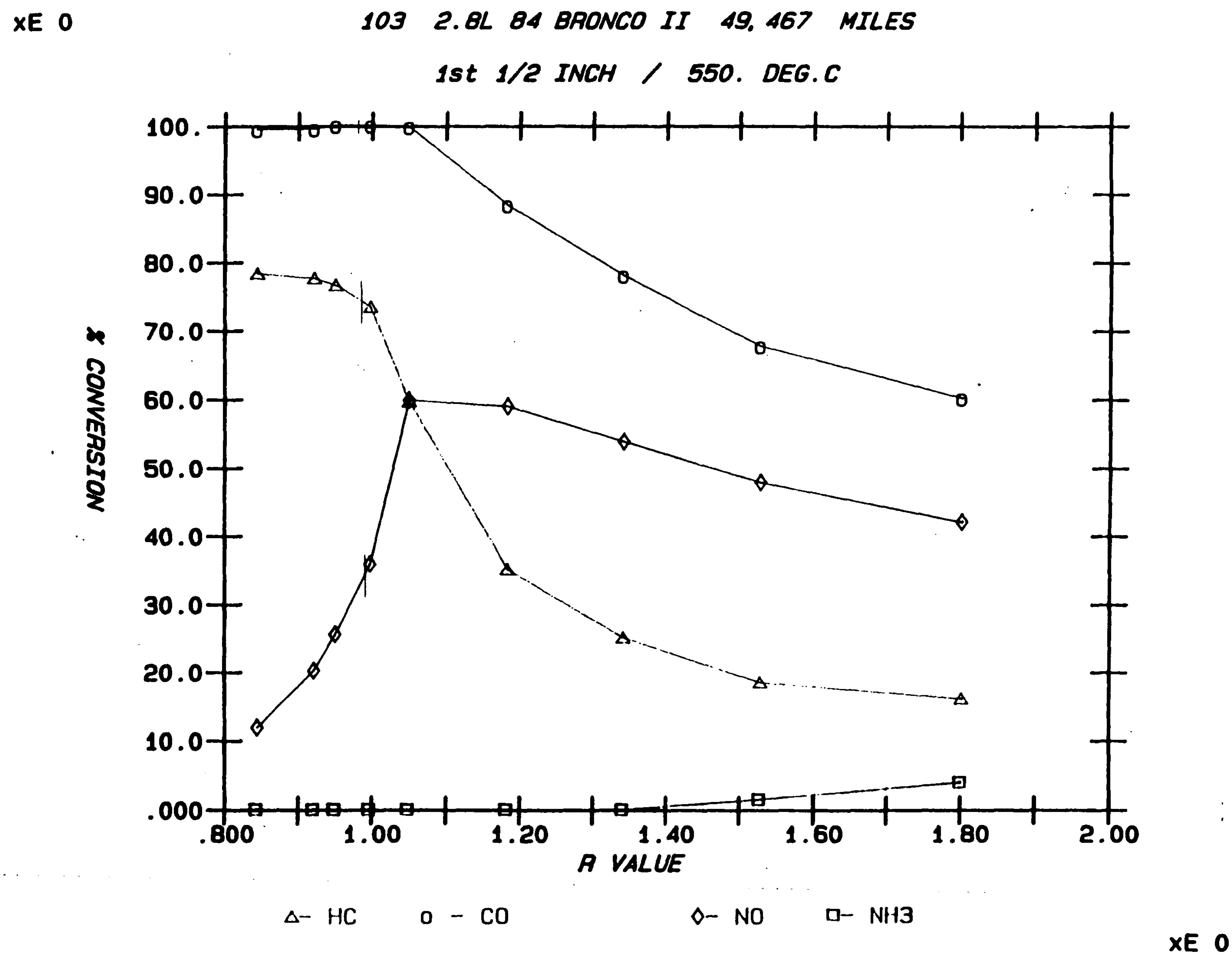
138

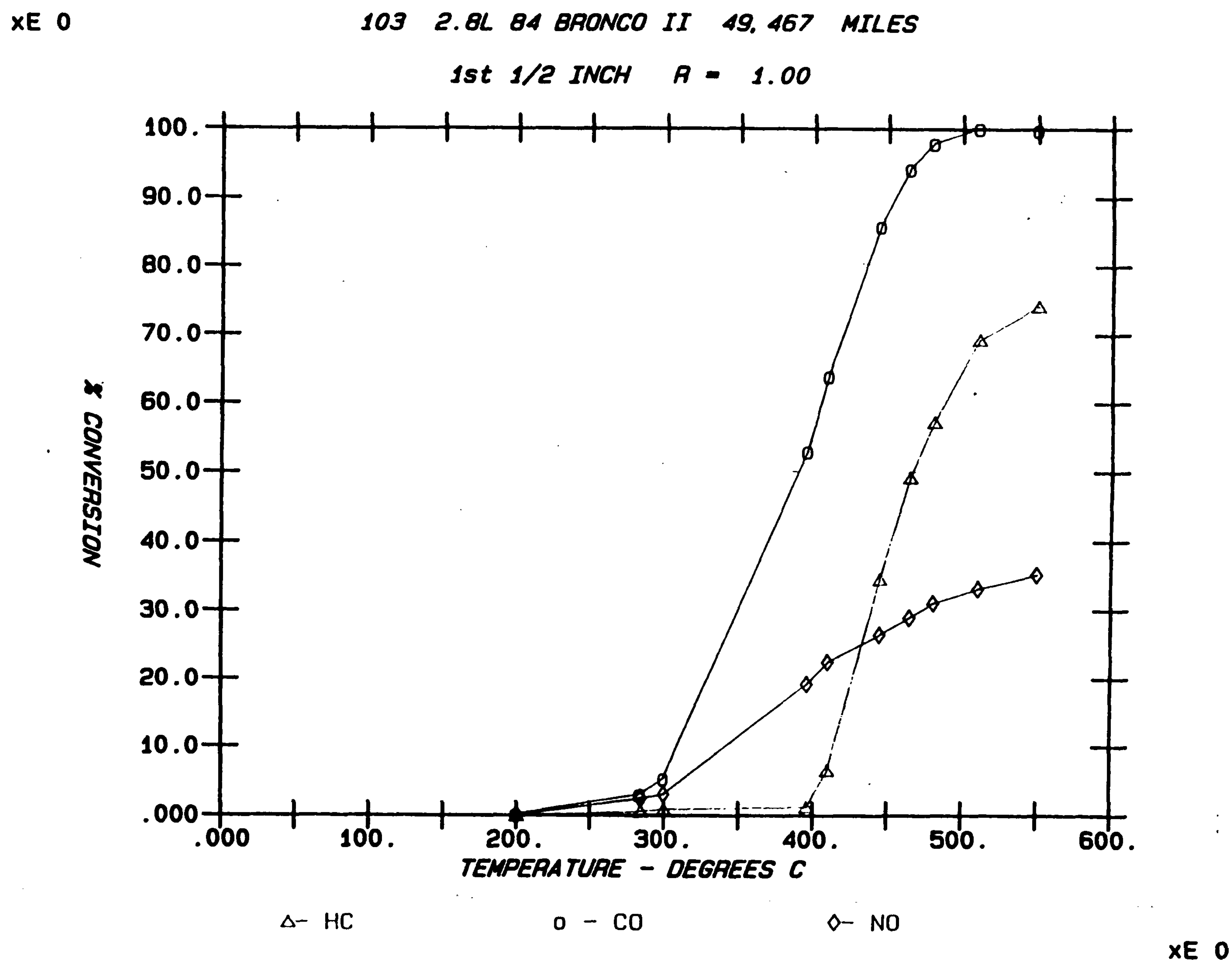


xE 0
102 2.3L 84 TEMPO HSC 47,149 MILES
1st BRICK INLET / 548. DEG.C
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
Δ– HC
o – CO
◊– NO
□– NH3
xE 0


xE 0
102 2.3L 84 TEMPO HSC 47,149 MILES
1st BRICK INLET R = 1.00
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ- HC
o - CO
◊- NO
xE 0

140

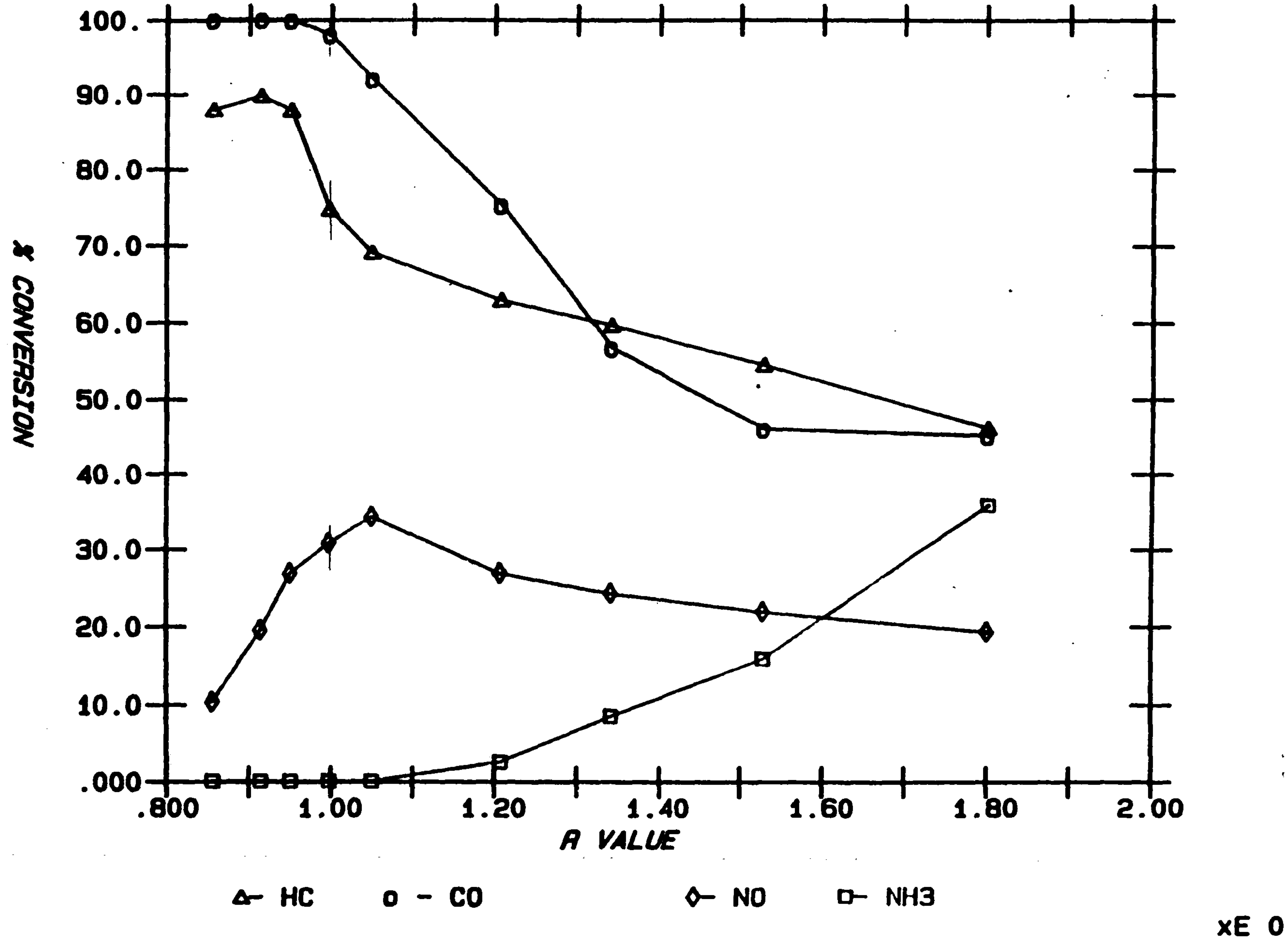

xE 0
103 2.8L 84 BRONCO II 49,467 MILES
1st 1/2 INCH / 550. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
△– HC
o – CO
◇– NO
□– NH3
xE 0


xE 0
103 2.8L 84 BRONCO II 49,467 MILES
1st 1/2 INCH R = 1.00
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
△- HC
o - CO
◇- NO
xE 0

xE 0

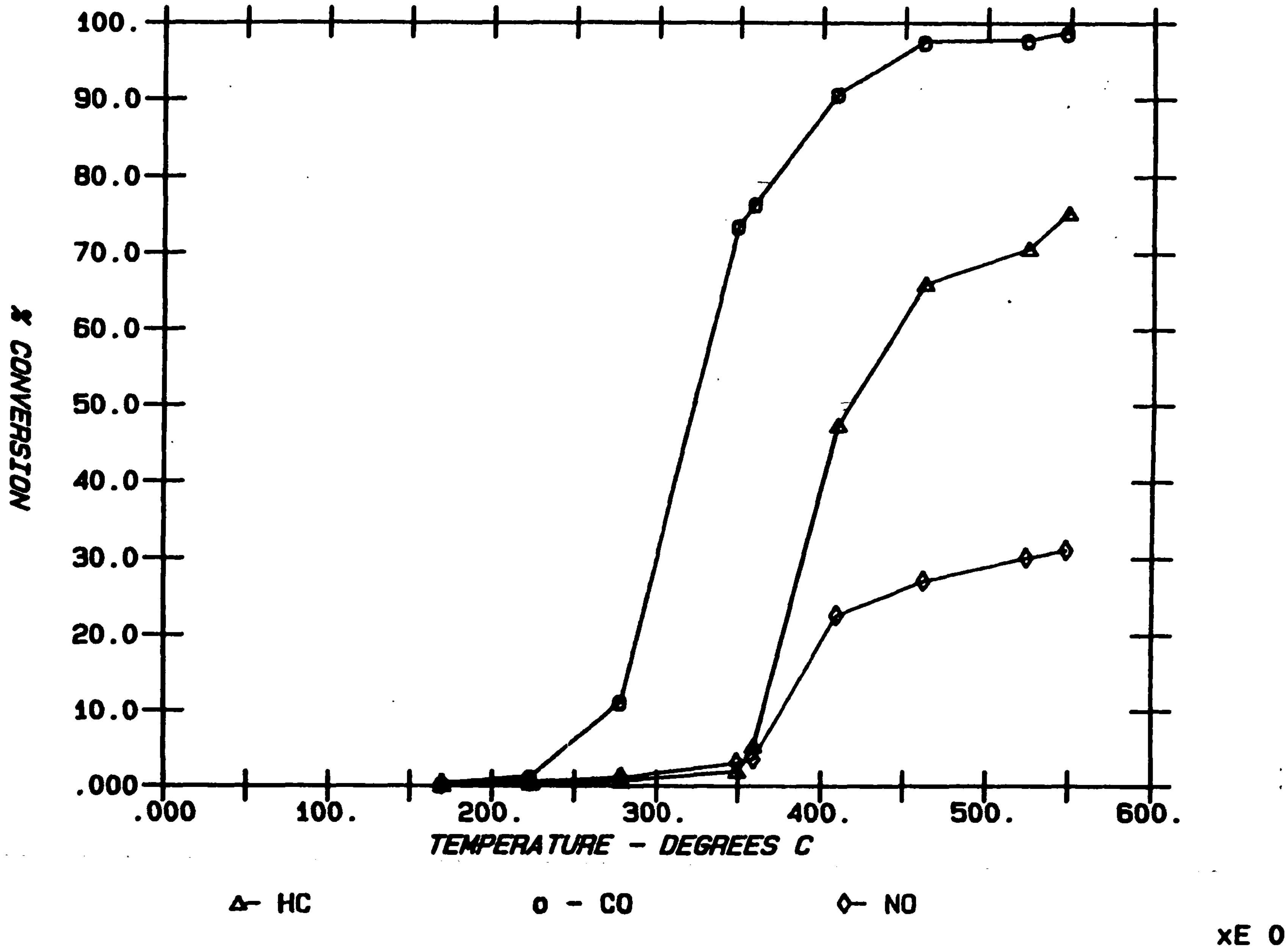
104 1.9L 86 ESCORT EFI 32,319 MILES

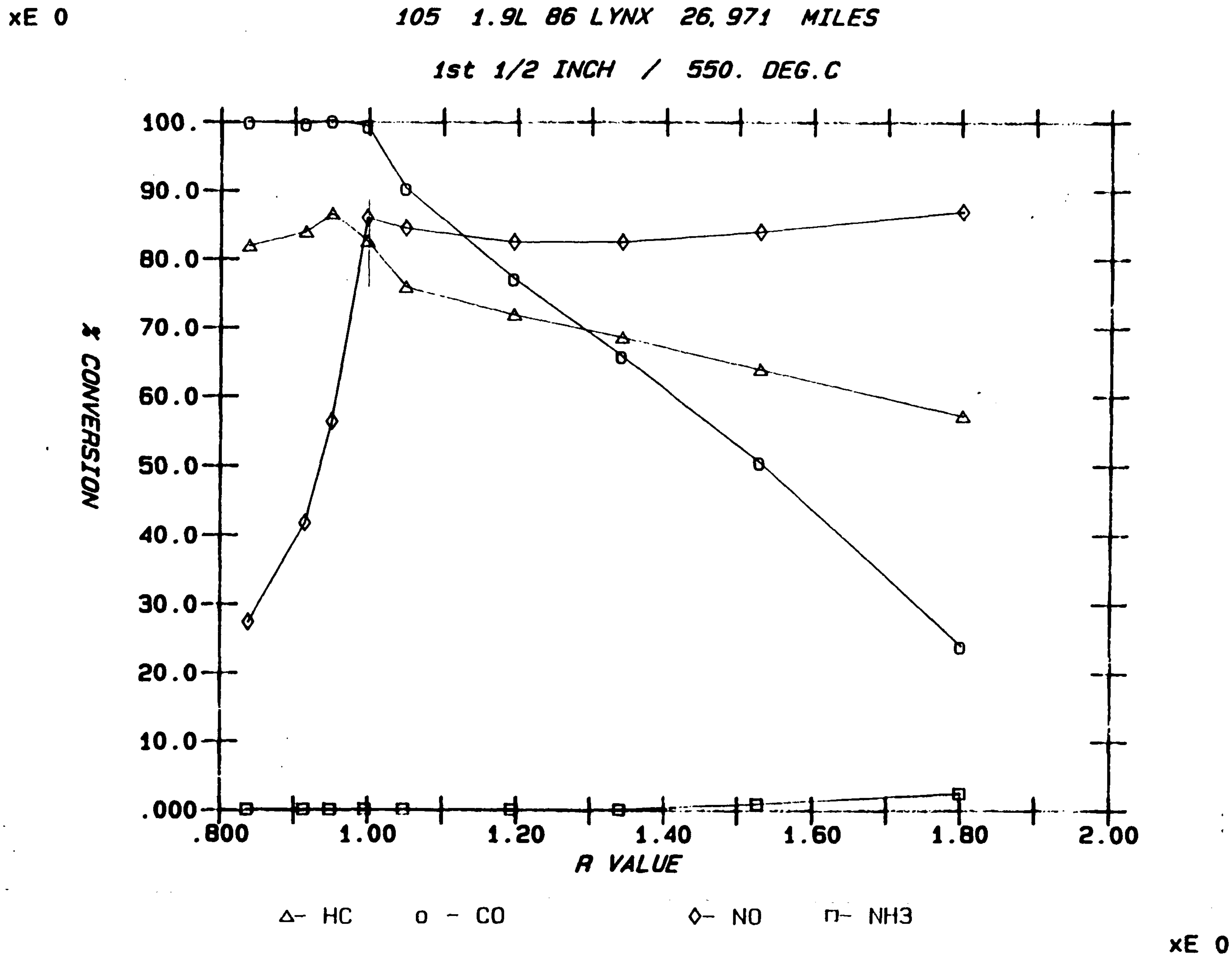
1st BRICK INLET / 550. DEG.C



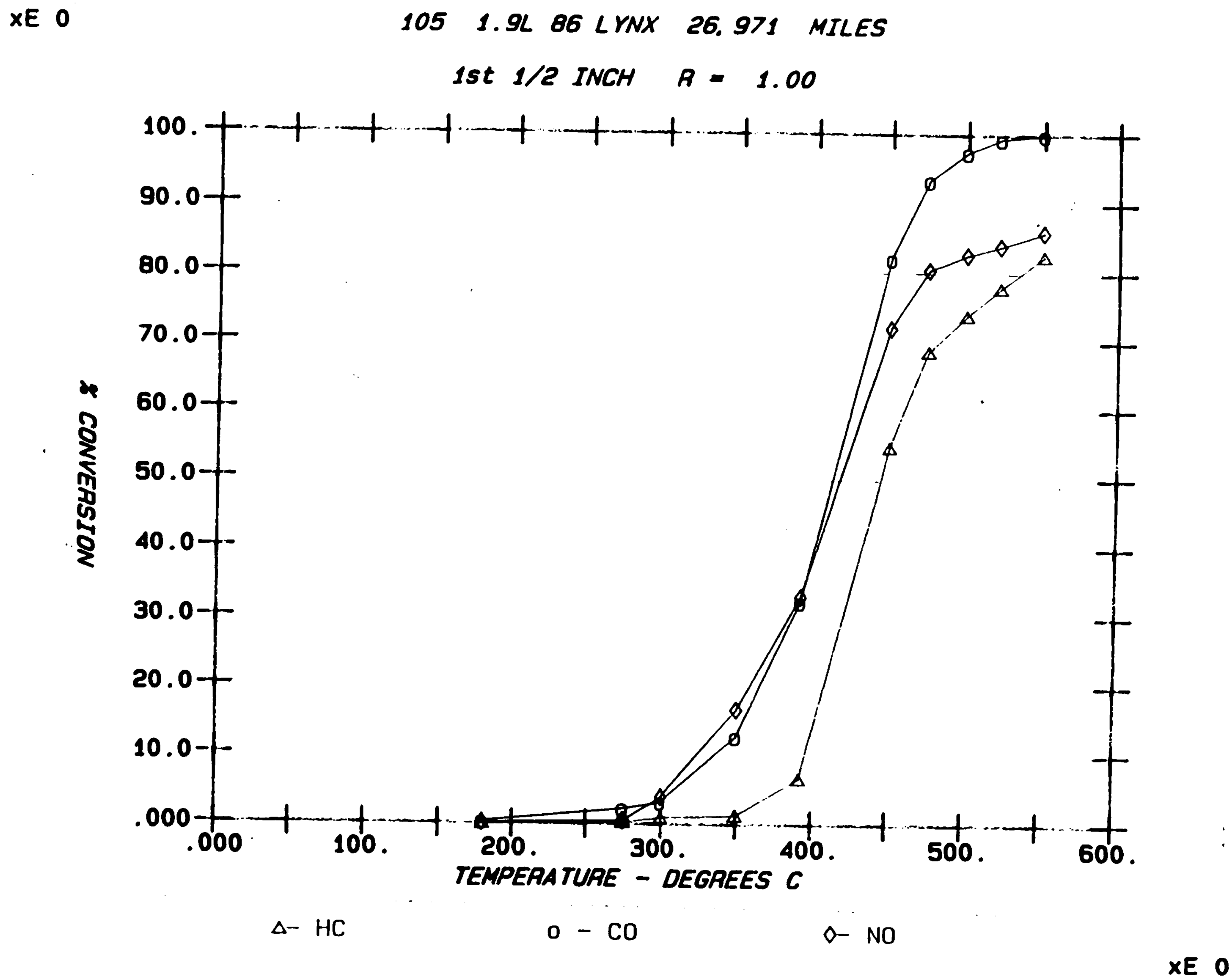
104 1.9L 86 ESCORT EFI 32,319 MILES

1st BRICK INLET R = 1.00



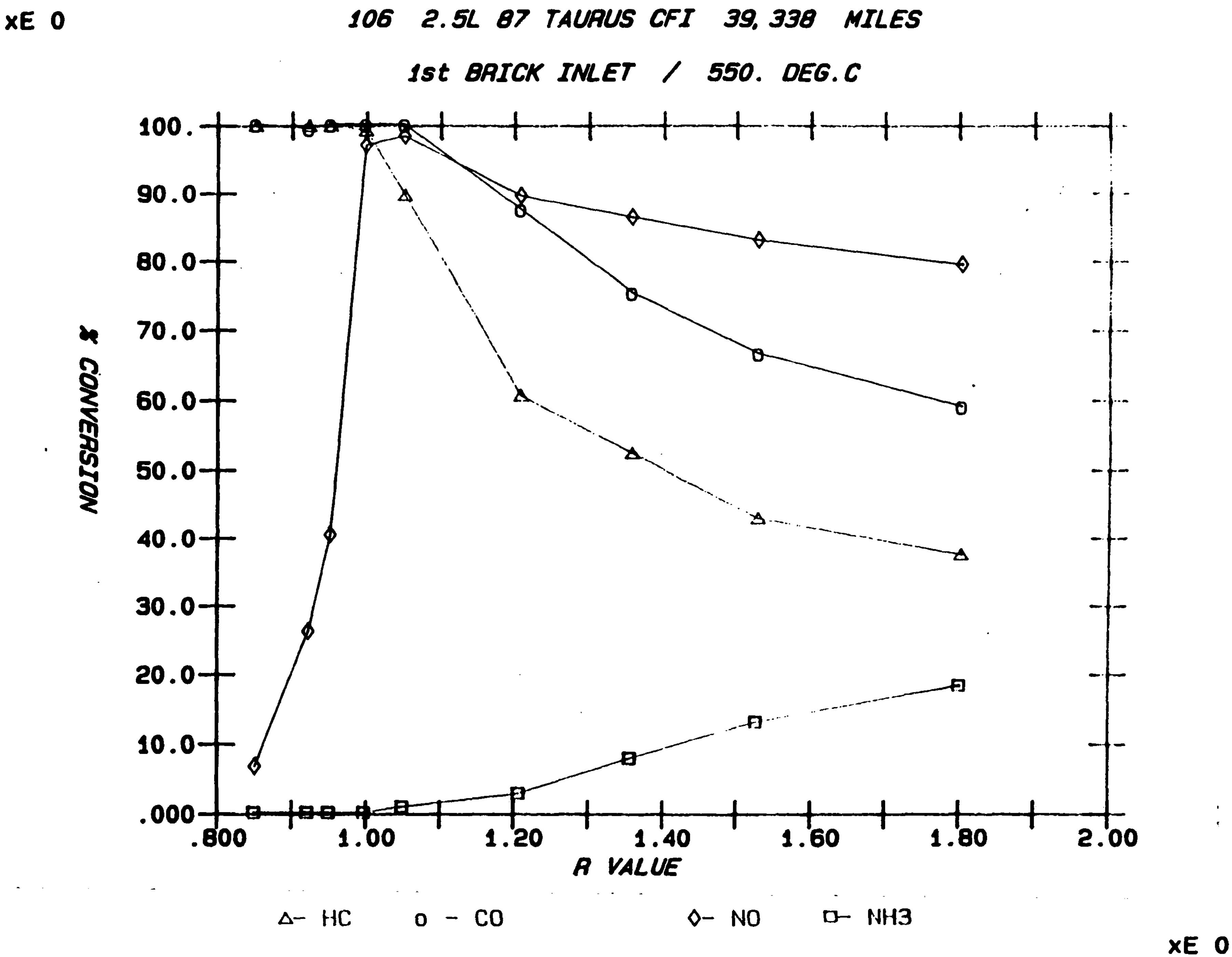

xE 0
105 1.9L 86 LYNX 26,971 MILES
1st 1/2 INCH / 550. DEG.C
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
△– HC
o – CO
◇– NO
□– NH3
xE 0

145



xE 0
105 1.9L 86 LYNX 26,971 MILES
1st 1/2 INCH R = 1.00
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
△- HC
o - CO
◇- NO
xE 0

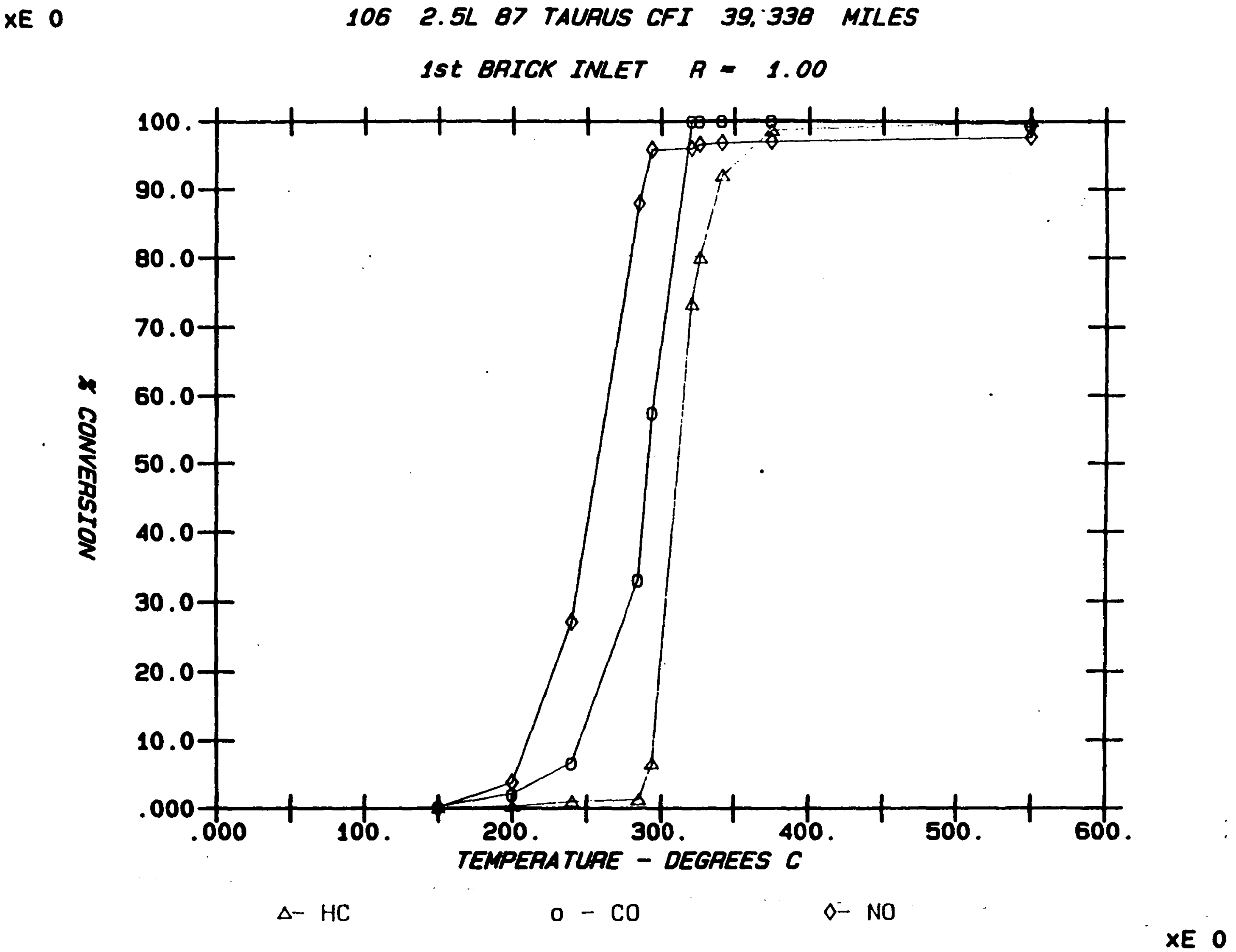
146

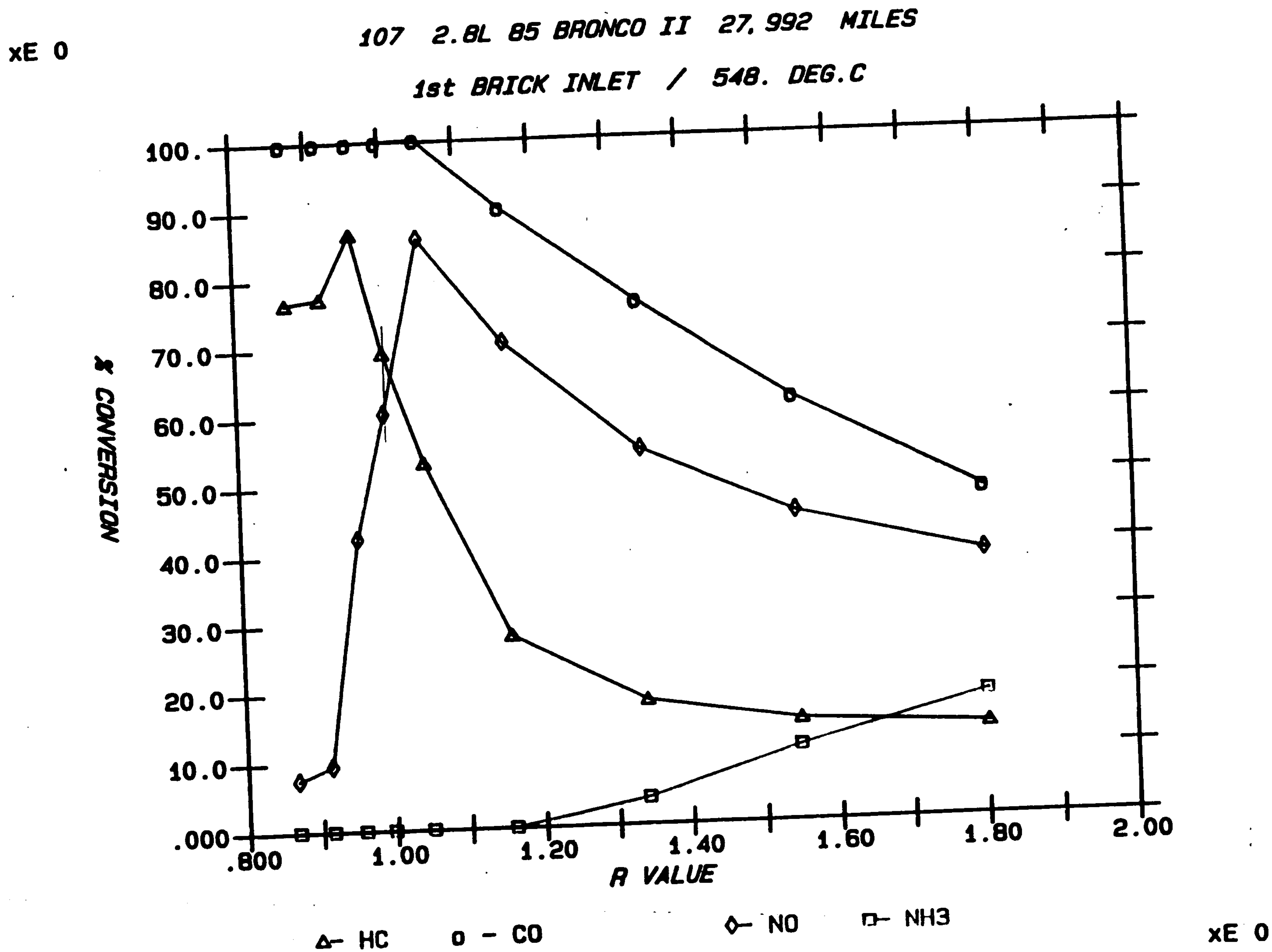

xE 0
106 2.5L 87 TAURUS CFI 39,338 MILES
1st BRICK INLET / 550. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
△– HC
o – CO
◇– NO
□– NH3
xE 0

P 42

106 2.5L 87 TAURUS CFI 39,338 MILES

1st BRICK INLET R = 1.00

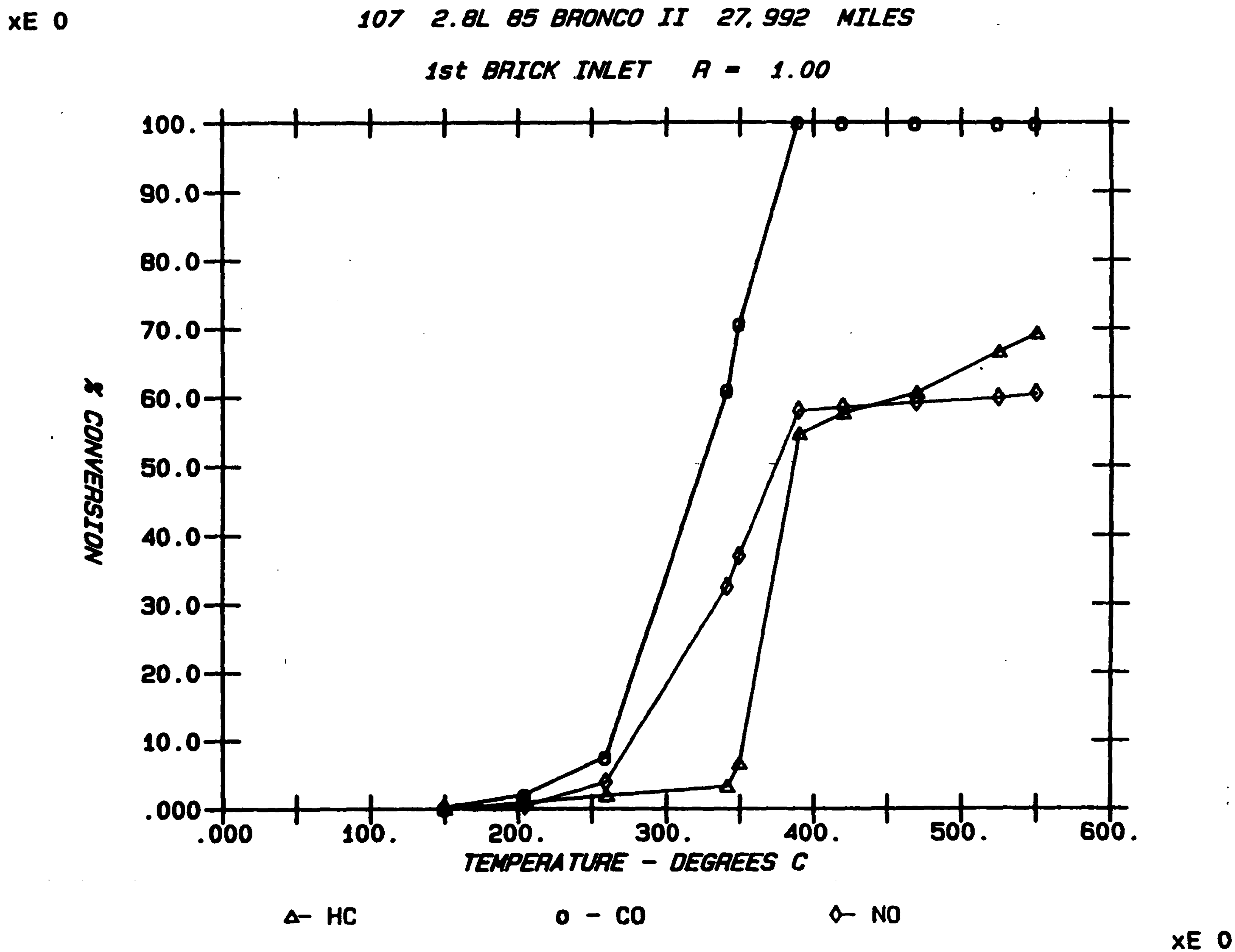


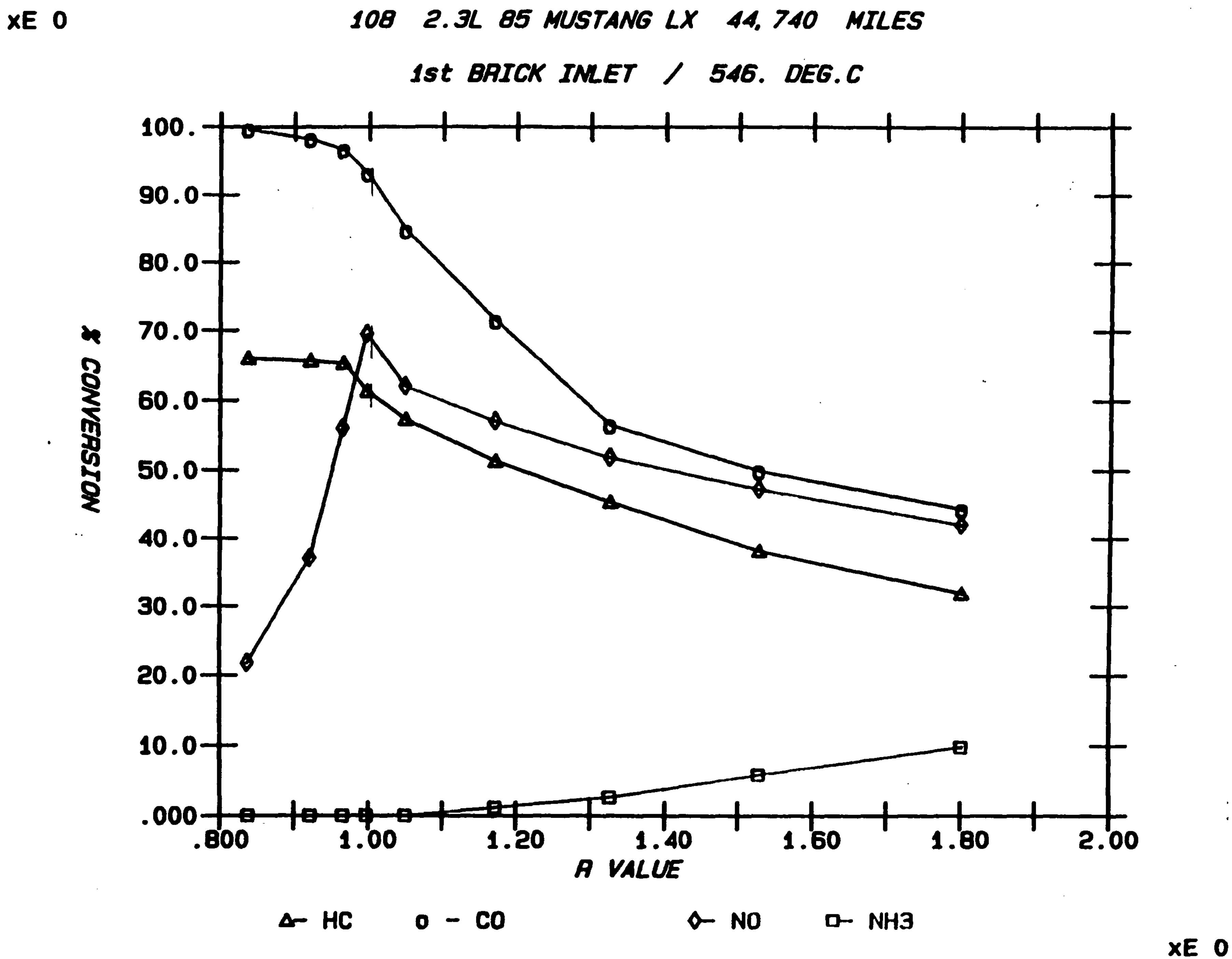

107 2.8L 85 BRONCO II 27,992 MILES
1st BRICK INLET / 548. DEG.C
xE 0
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
xE 0
HC
CO
NO
NH3

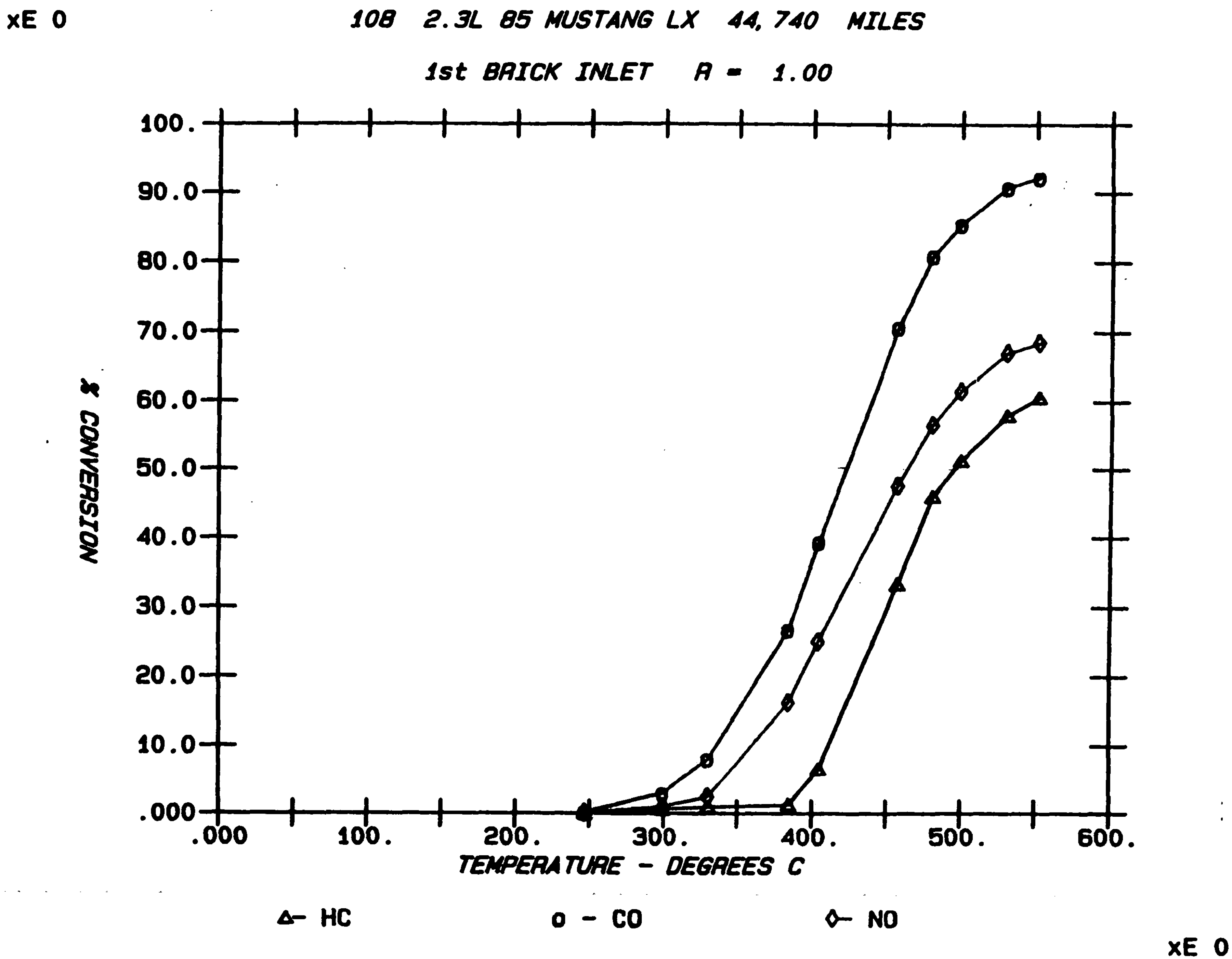
149

107 2.8L 85 BRONCO II 27,992 MILES

1st BRICK INLET R = 1.00

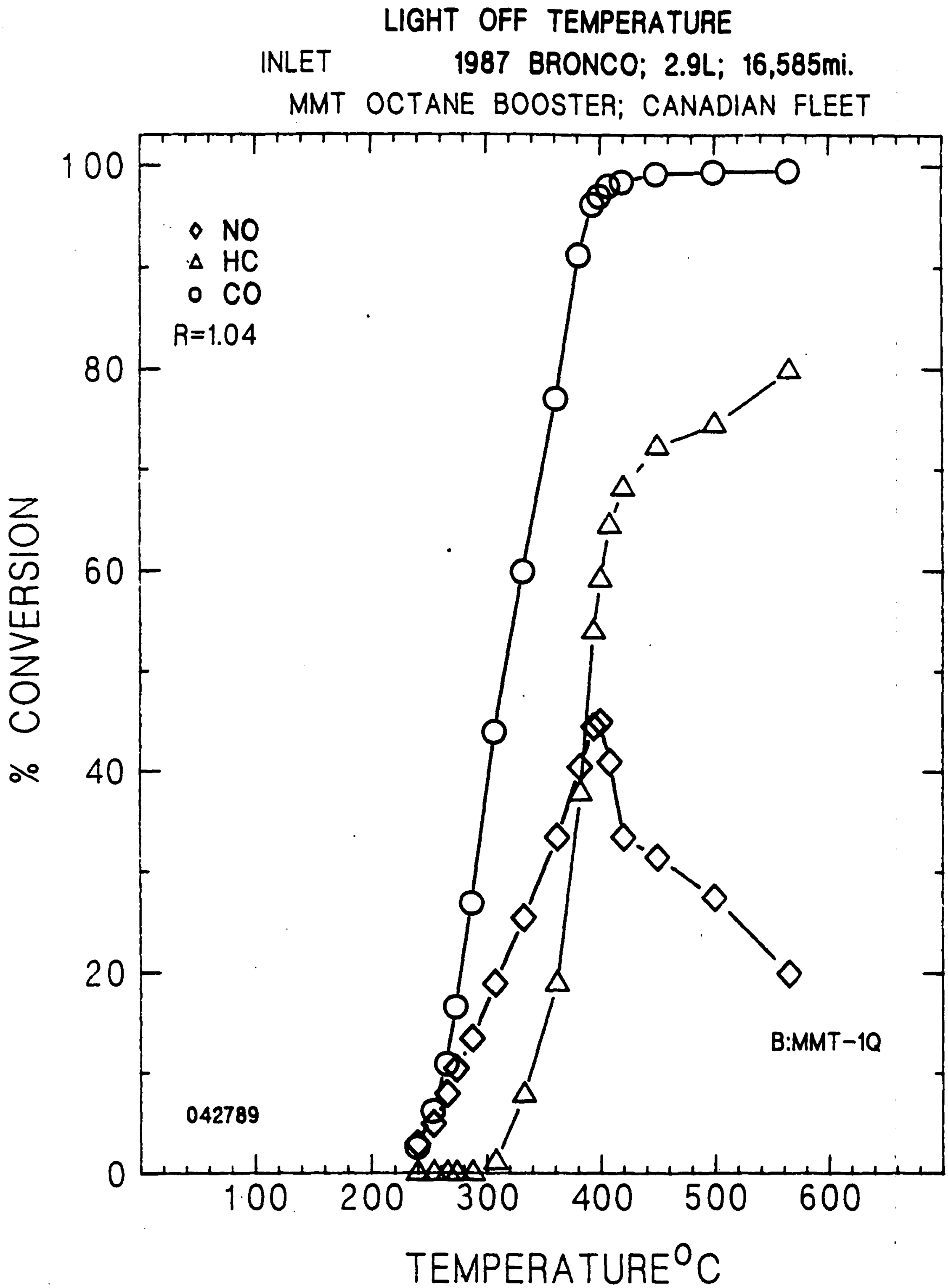



xE 0
108 2.3L 85 MUSTANG LX 44,740 MILES
1st BRICK INLET / 546. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
A VALUE
Δ- HC
o - CO
◇- NO
□- NH3
xE 0

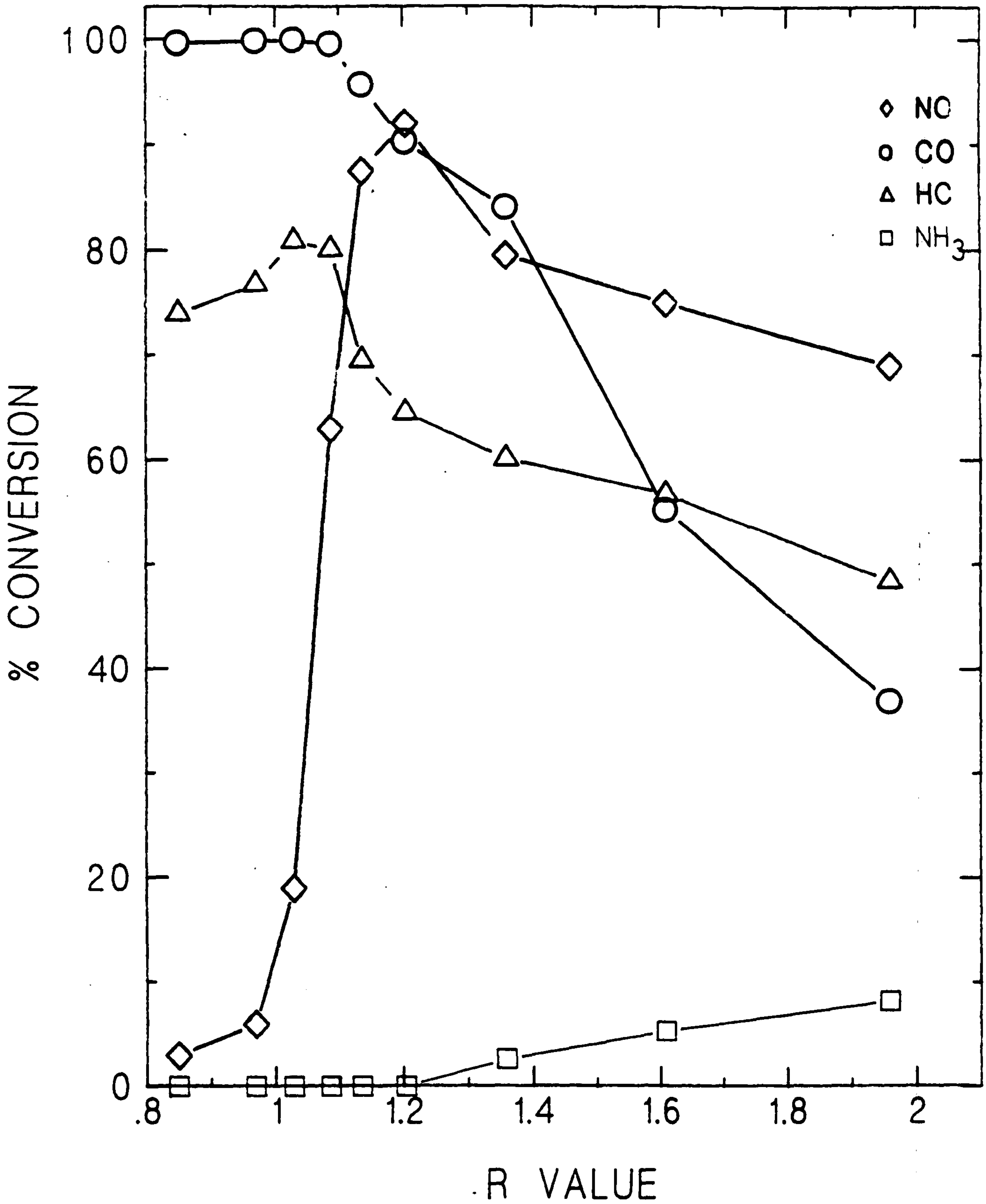


xE 0
108 2.3L 85 MUSTANG LX 44,740 MILES
1st BRICK INLET R = 1.00
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ– HC
o – CO
◊– NO
xE 0

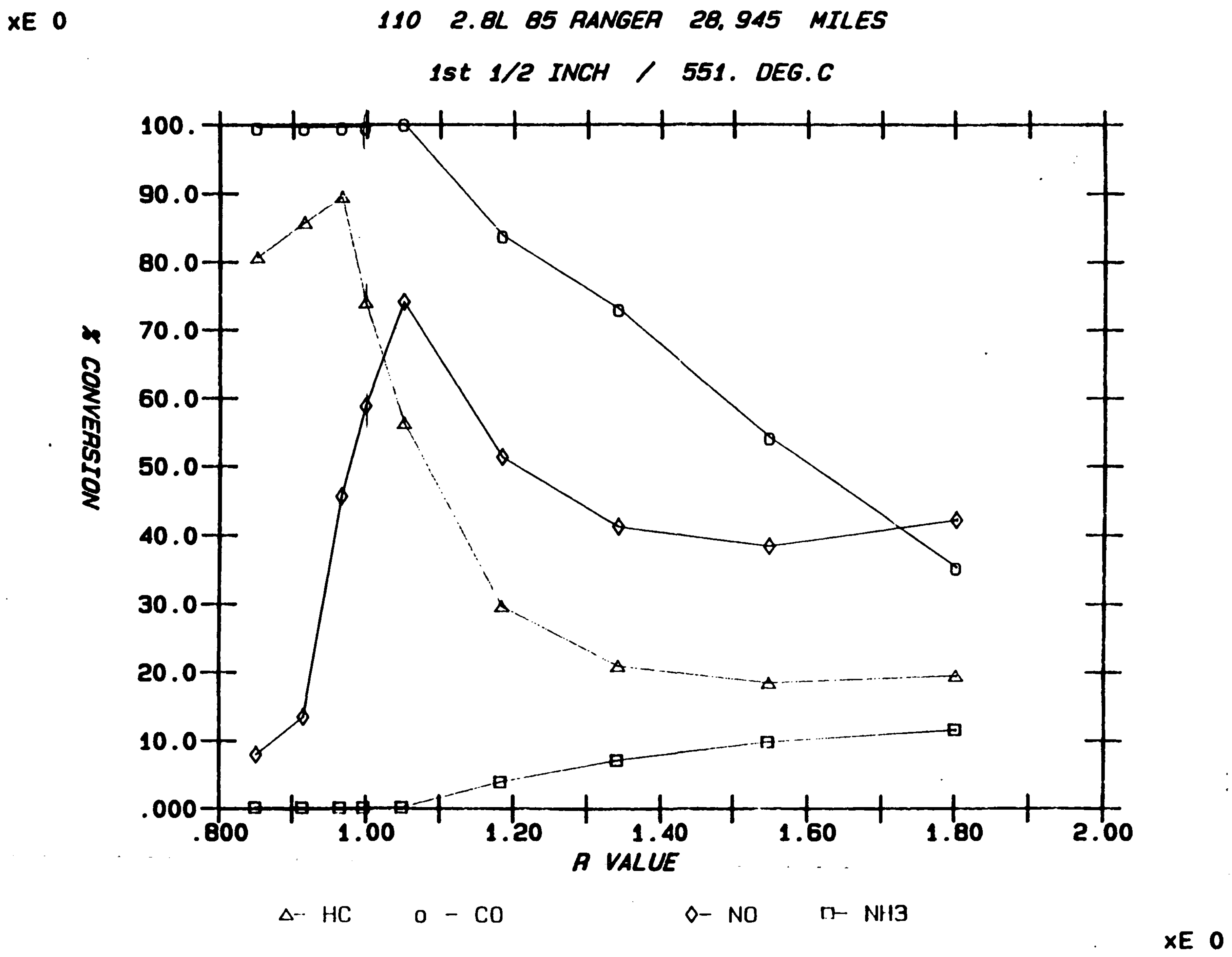
152


LIGHT OFF TEMPERATURE
INLET
1987 BRONCO; 2.9L; 16,585mi.
MMT OCTANE BOOSTER; CANADIAN FLEET
NO
HC
CO
R=1.04
100
80
60
40
20
0
% CONVERSION
042789
B:MMT-1Q
100
200
300
400
500
600
TEMPERATURE°C

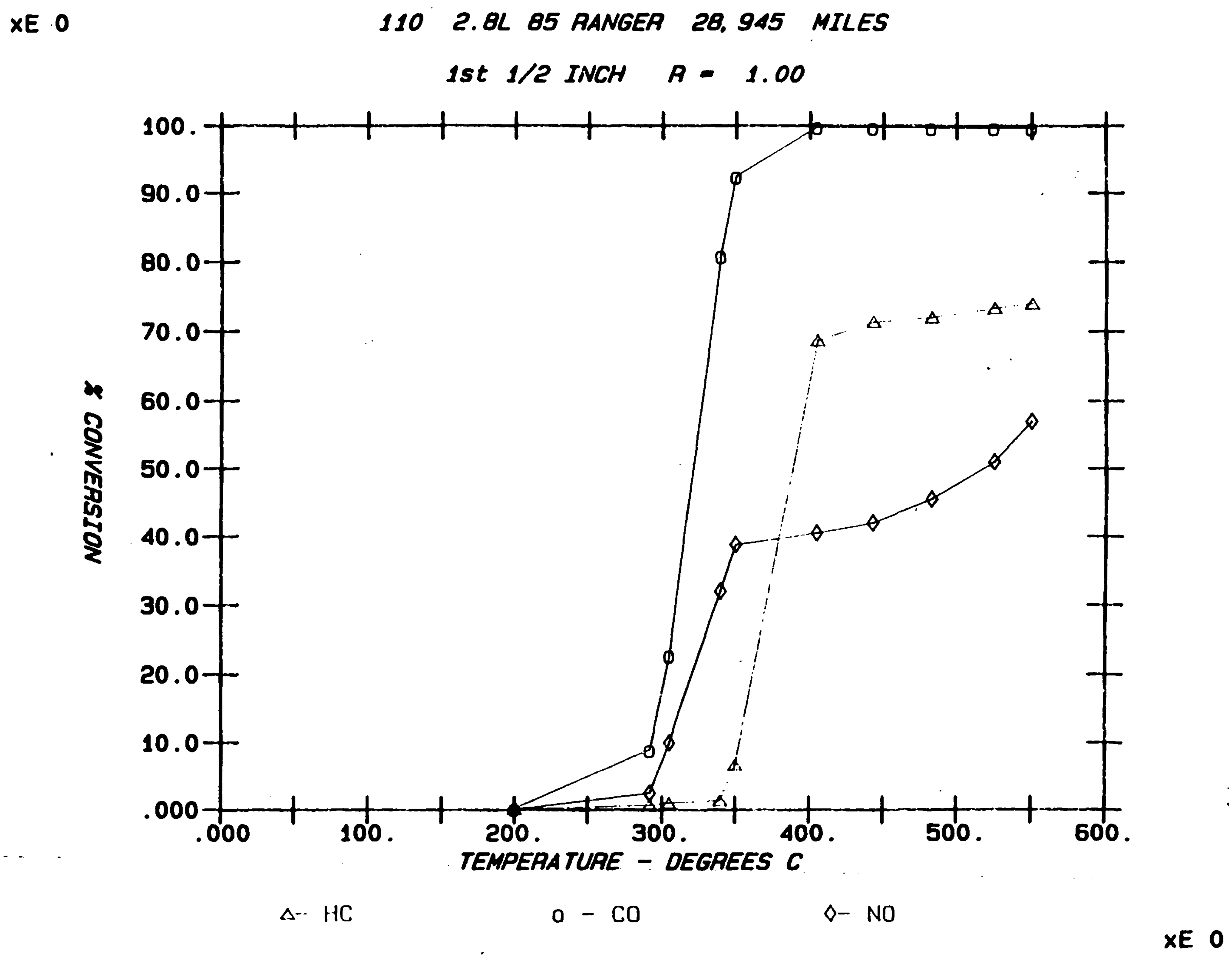
STEADY-STATE FOR: INLET 1987 BRONCO; 2.9L; 16,585mi.
MMT OCTANE BOOSTER; CANADIAN FLEET

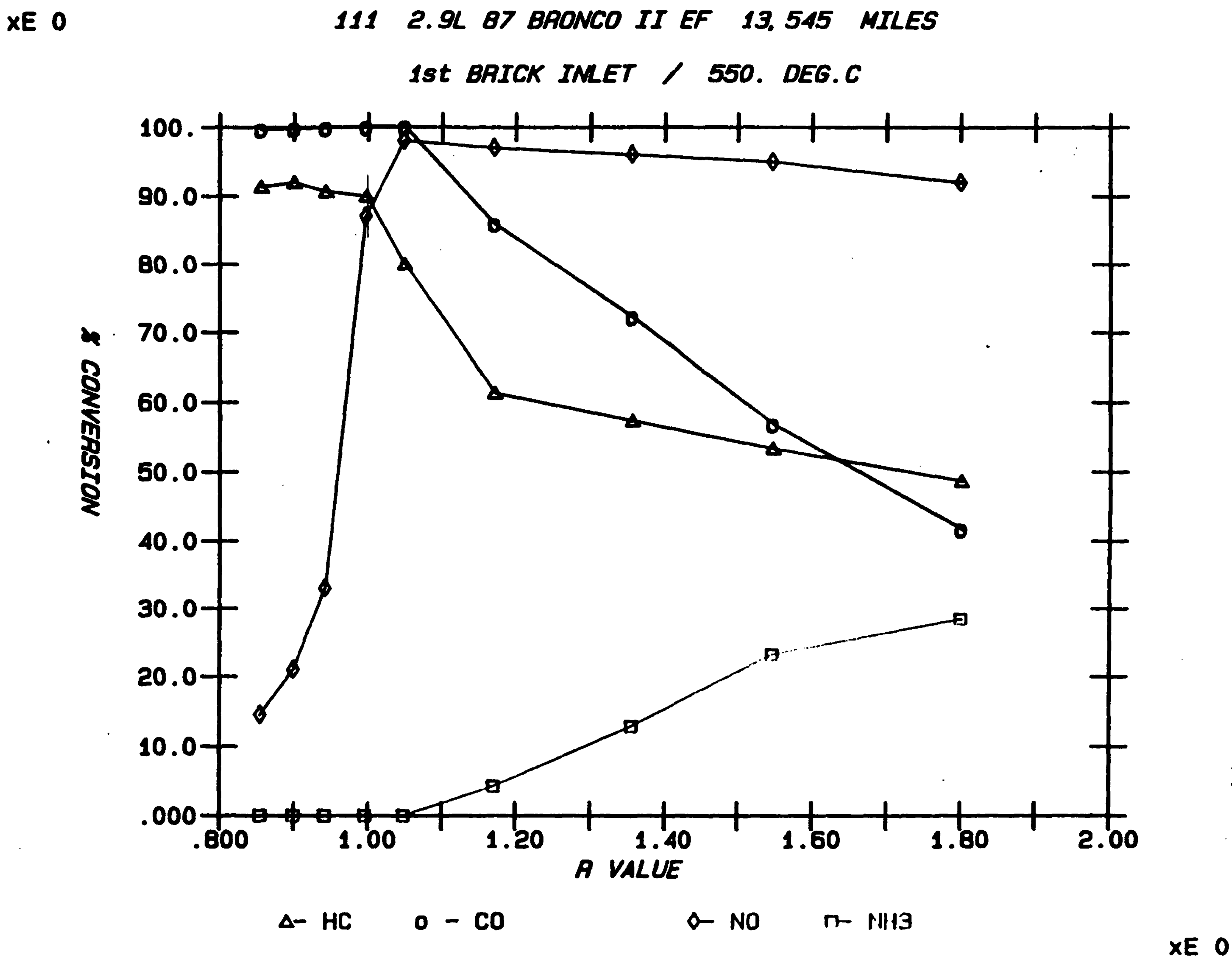


B:MMT-1P


xE 0
110 2.8L 85 RANGER 28,945 MILES
1st 1/2 INCH / 551. DEG.C
% CONVERSION
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
HC
CO
NO
NH3
xE 0

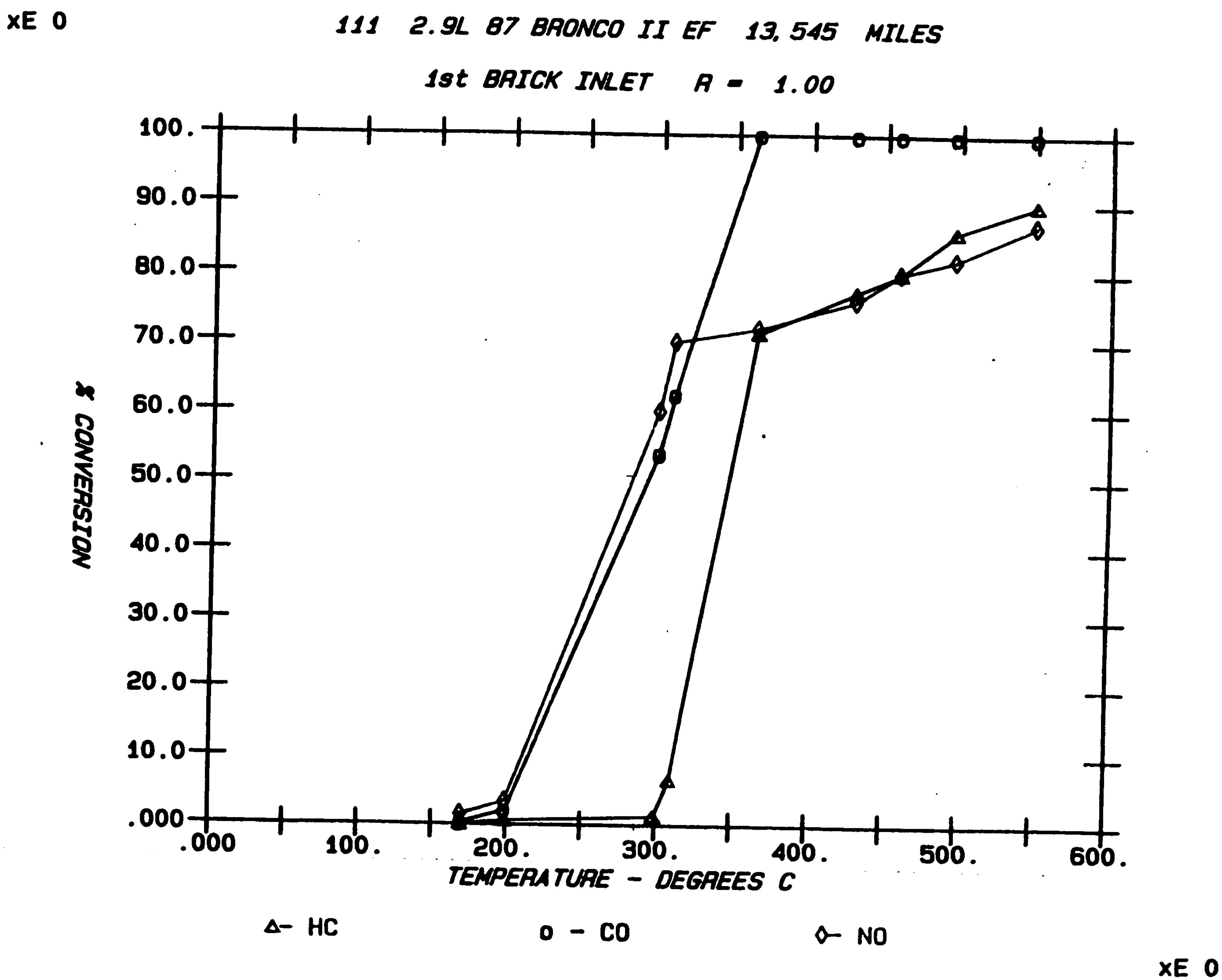
155


xE 0
110 2.8L 85 RANGER 28,945 MILES
1st 1/2 INCH R = 1.00
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
△- HC
o - CO
◇- NO
xE 0



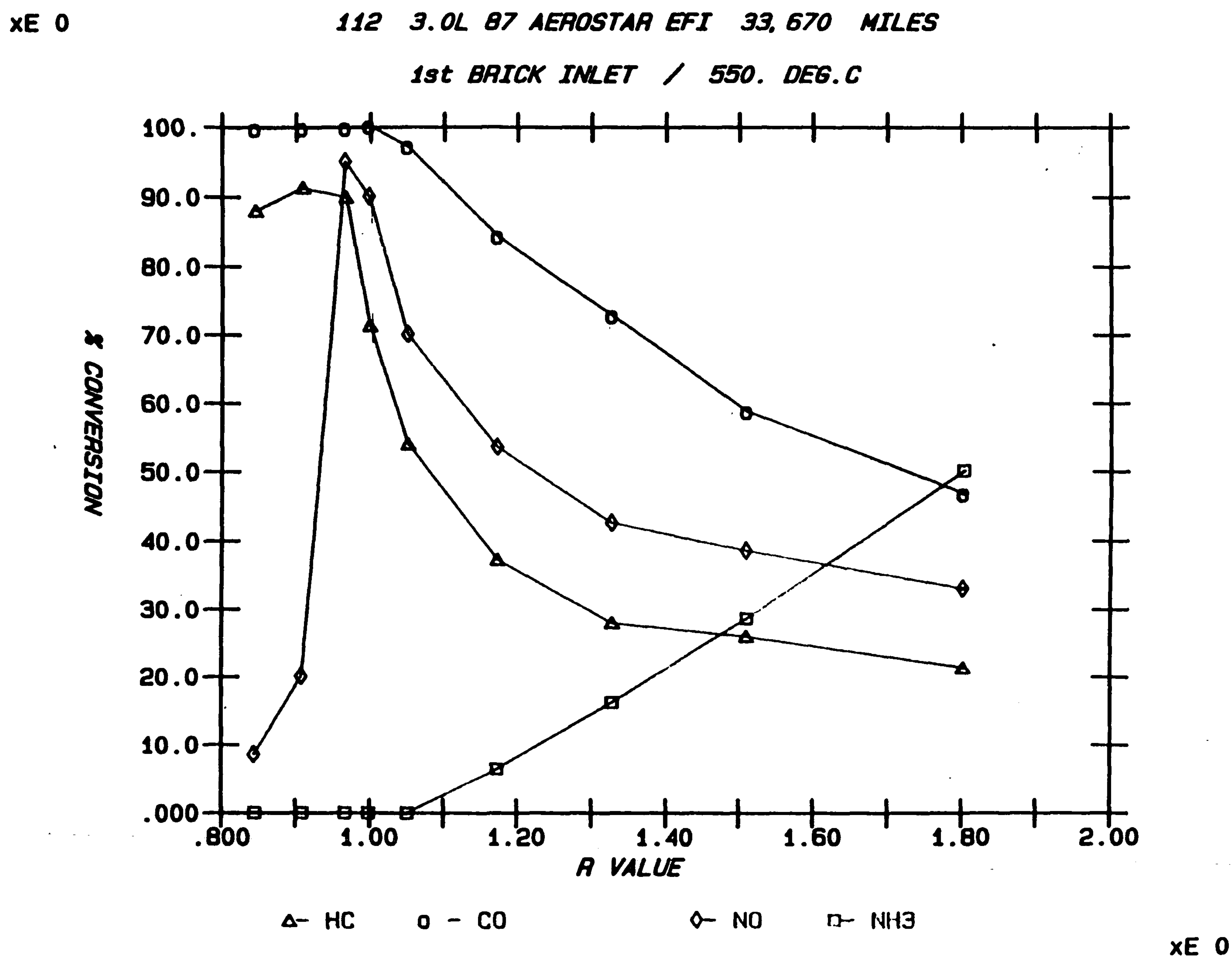
xE 0
111 2.9L 87 BRONCO II EF 13,545 MILES
1st BRICK INLET / 550. DEG.C
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
Δ- HC
o - CO
◇- NO
□- NH3
xE 0

157



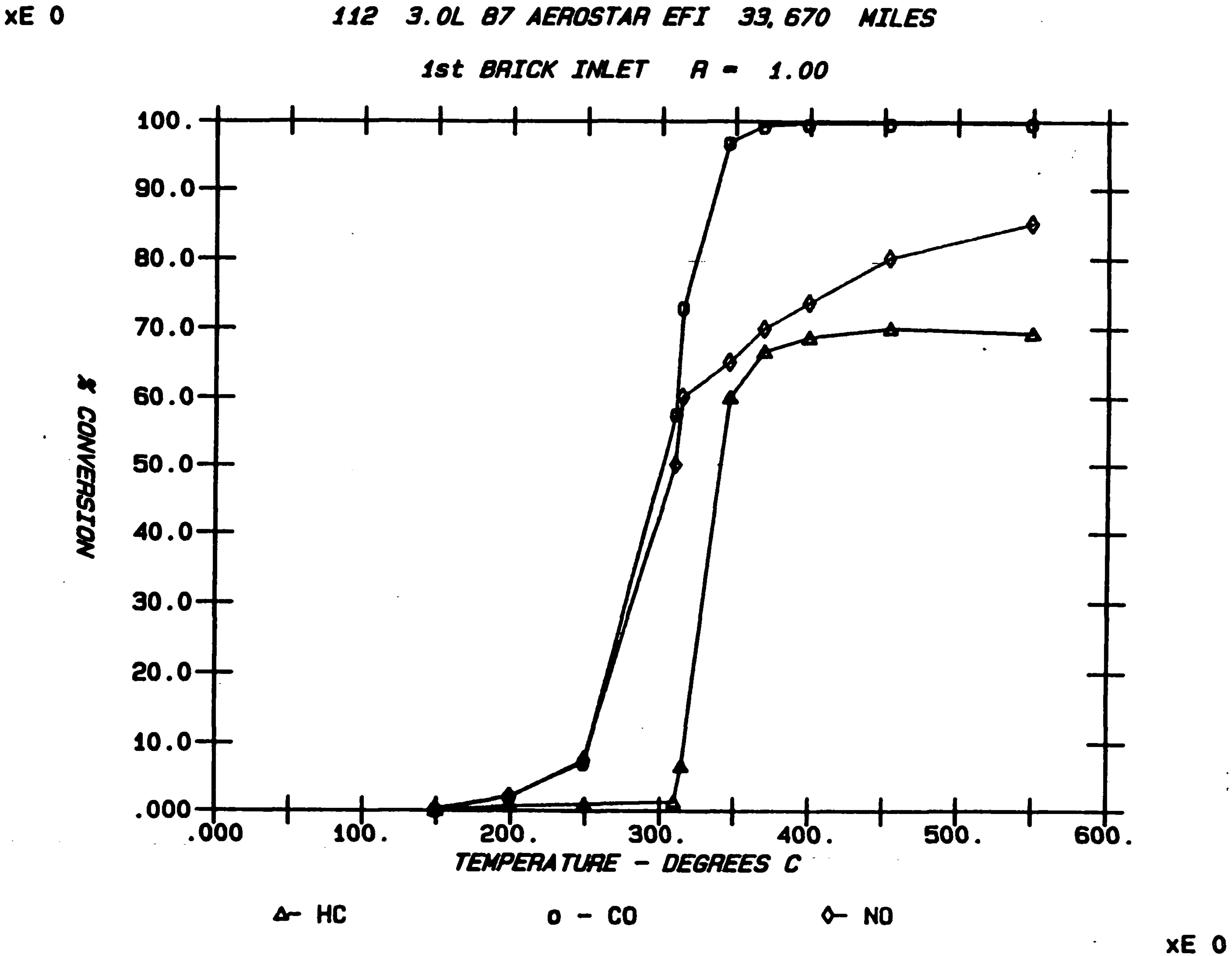
xE 0
111 2.9L 87 BRONCO II EF 13,545 MILES
1st BRICK INLET R = 1.00
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.000
100.
200.
300.
400.
500.
600.
TEMPERATURE - DEGREES C
Δ- HC
o - CO
◊- NO
xE 0

158



xE 0
112 3.0L 87 AEROSTAR EFI 33,670 MILES
1st BRICK INLET / 550. DEG.C
100.
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
.000
% CONVERSION
.800
1.00
1.20
1.40
1.60
1.80
2.00
R VALUE
△– HC
o – CO
◇– NO
□– NH3
xE 0

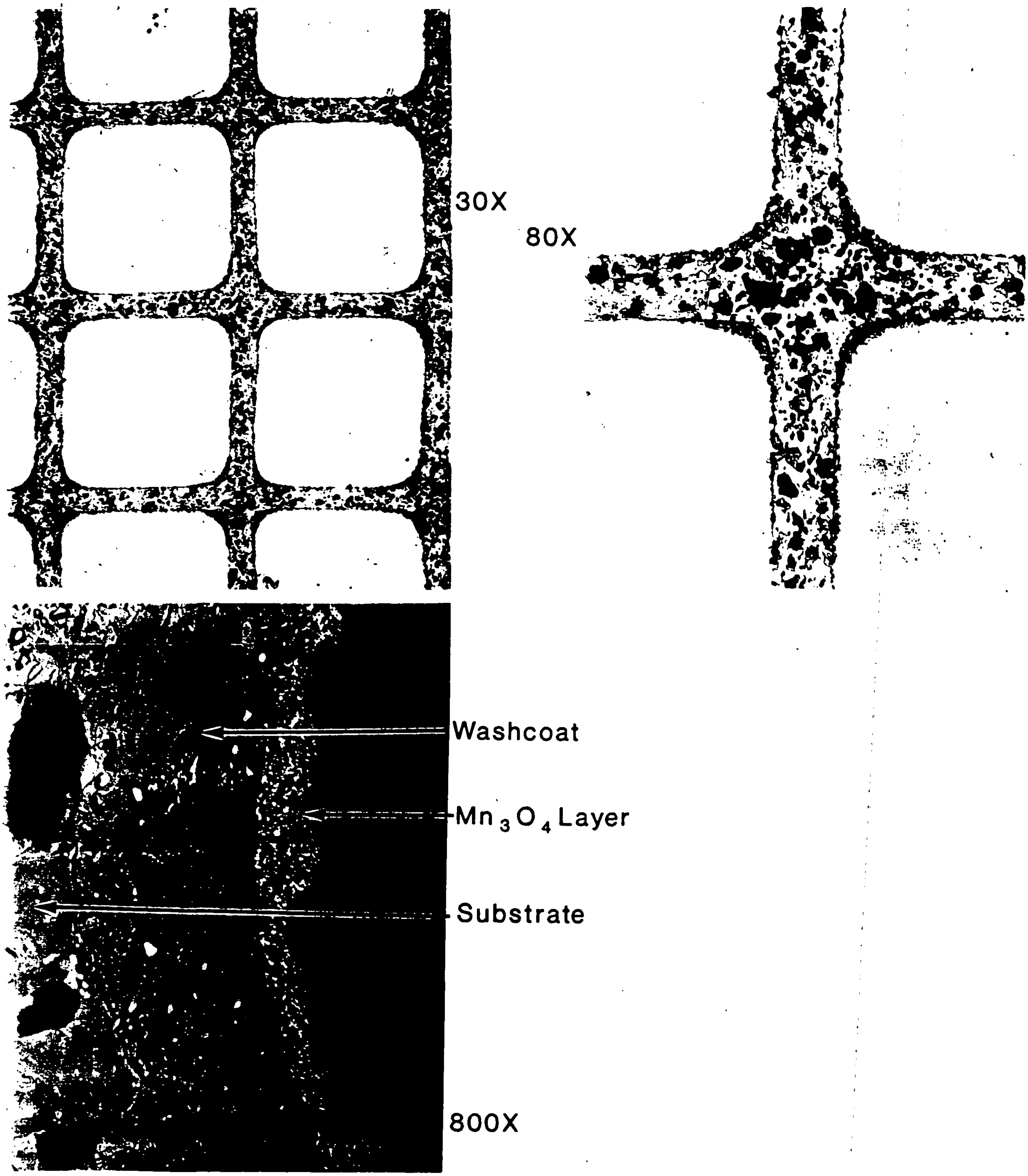
159



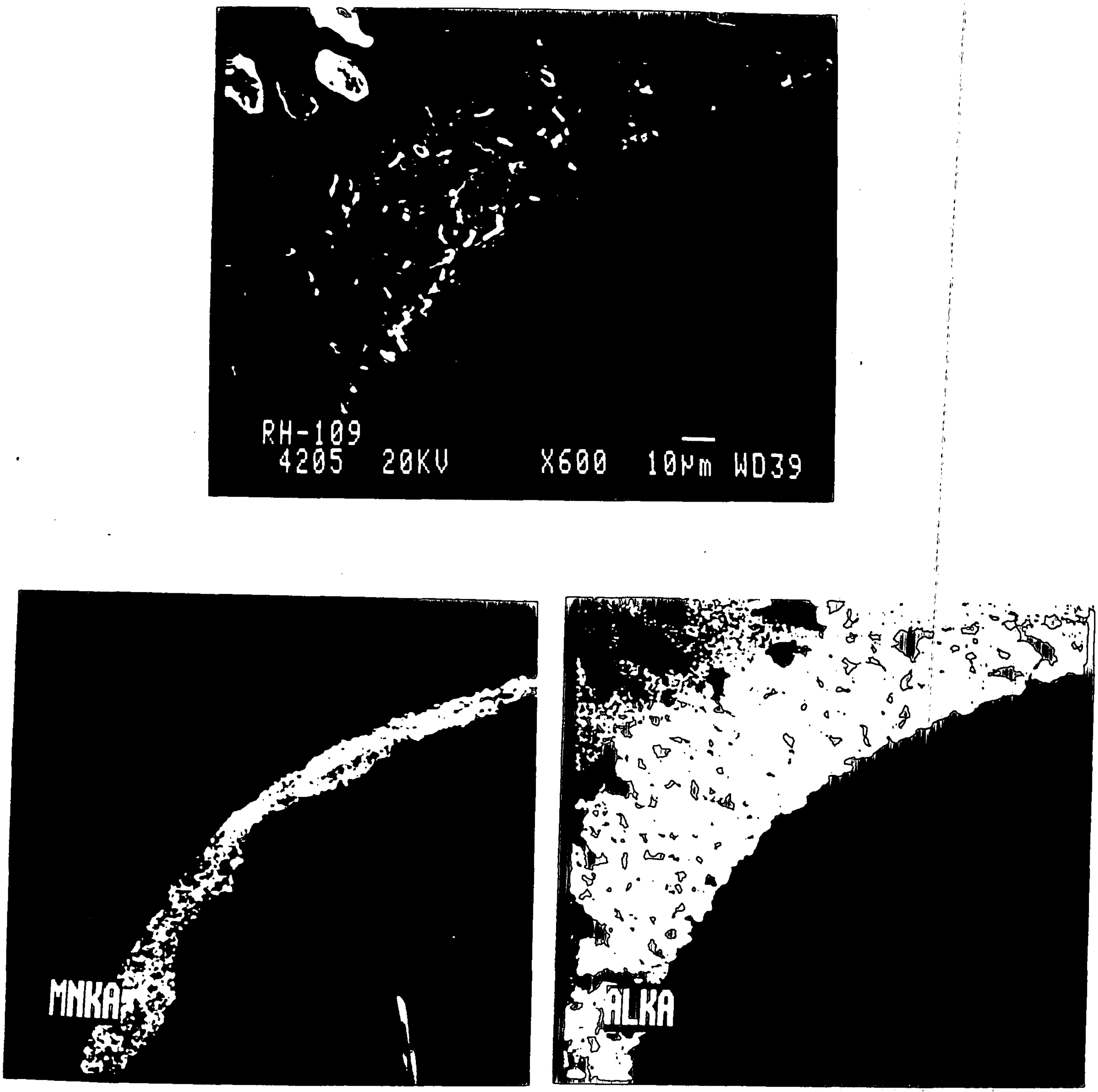
xE 0
112 3.0L 87 AEROSTAR EFI 33,670 MILES
1st BRICK INLET R = 1.00
% CONVERSION
TEMPERATURE - DEGREES C
HC
o - CO
NO
xE 0

160

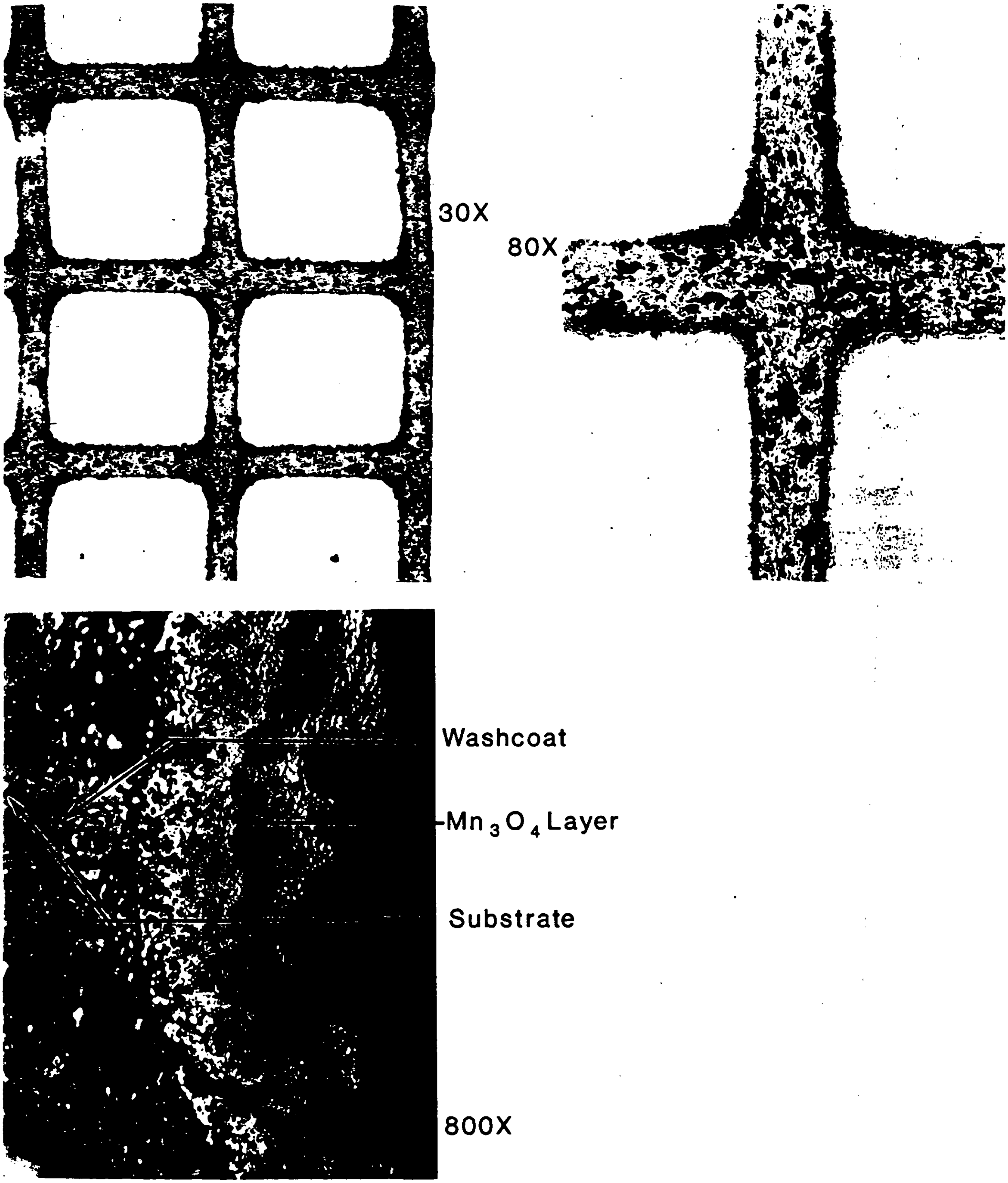
APPENDIX C
Optical and Scanning Electron Micrographs



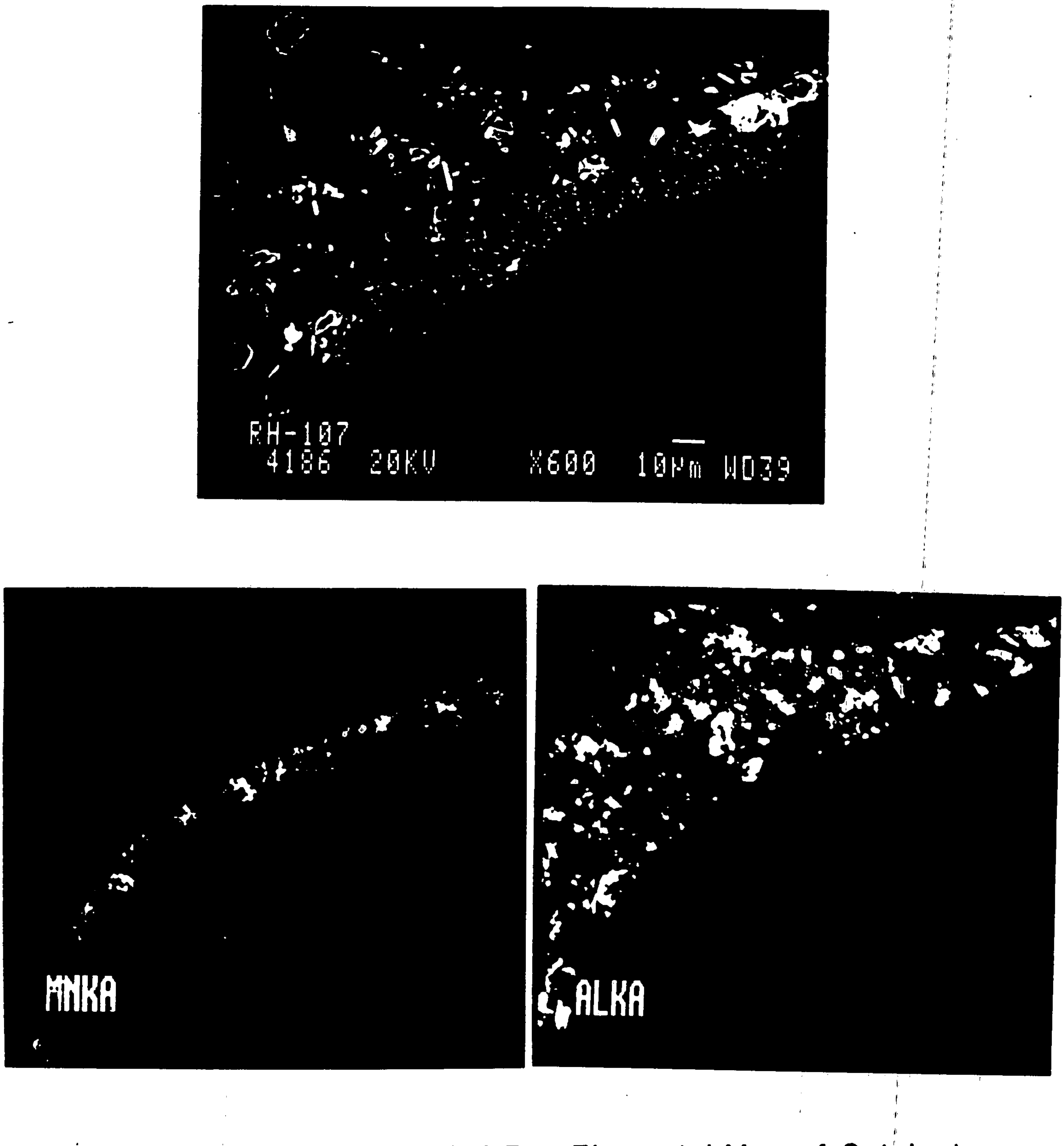
Optical Micrograph of Inlet of Catalyst with 16,585 miles



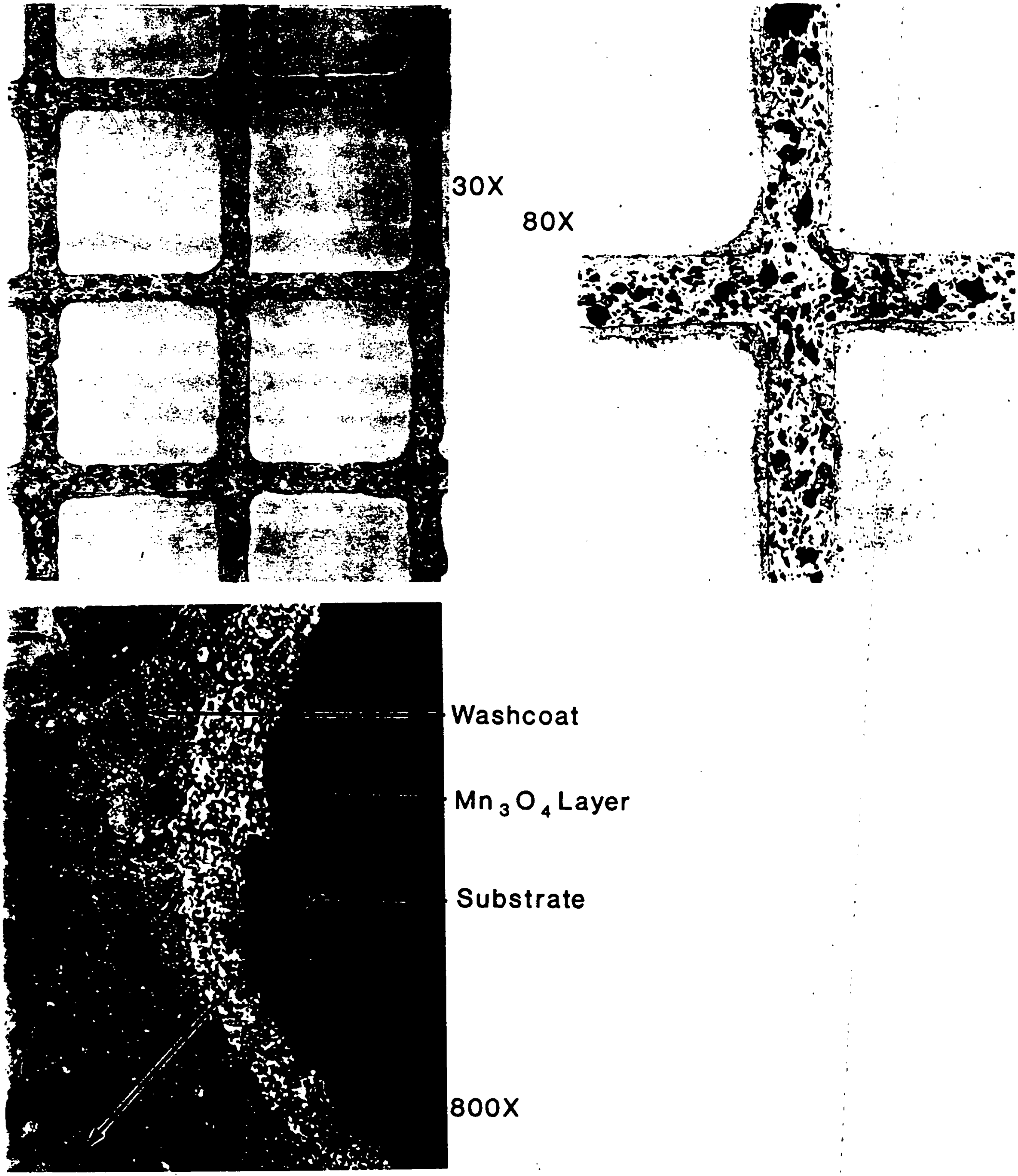
SEM Photomicrograph and X-Ray Elemental Map of Catalysts with 16,585 miles



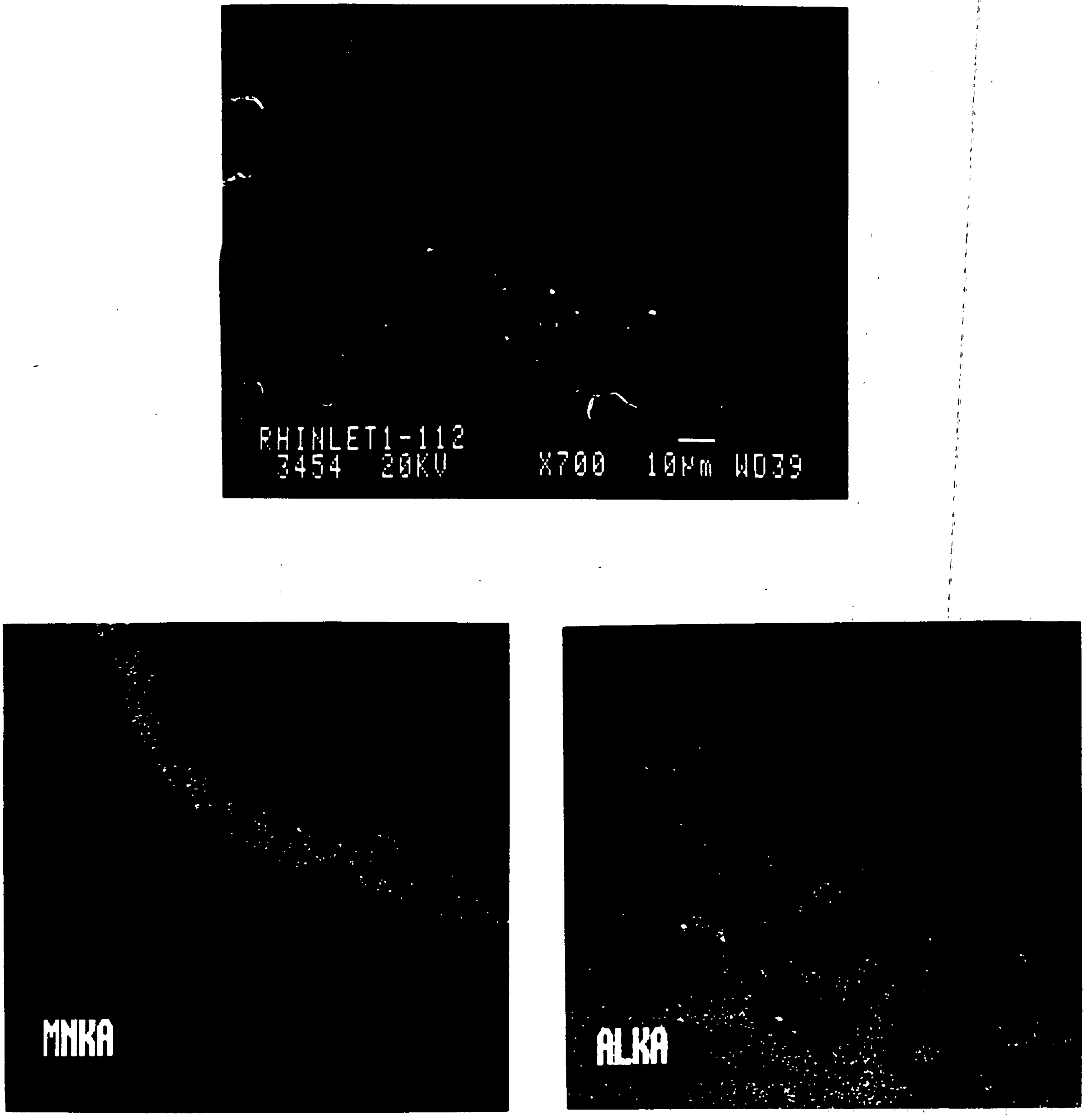
Optical Micrographs of Inlet of Catalysts with 27,992 miles



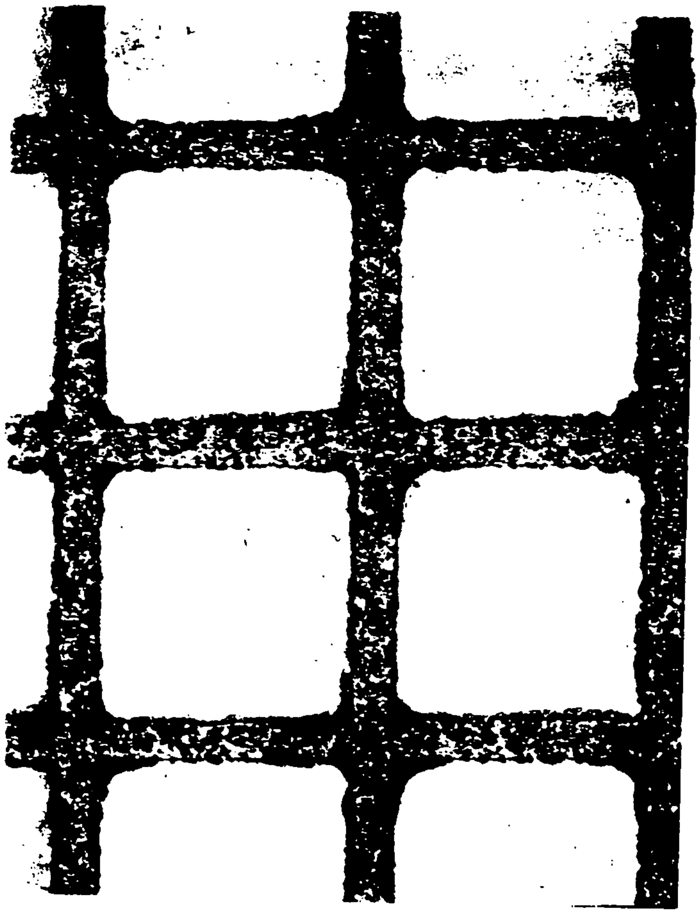
SEM Photomicrograph and X-Ray Elemental Map of Catalysts
with 27,992 miles



Optical Micrographs of Inlet of Catalysts with 33,679 miles

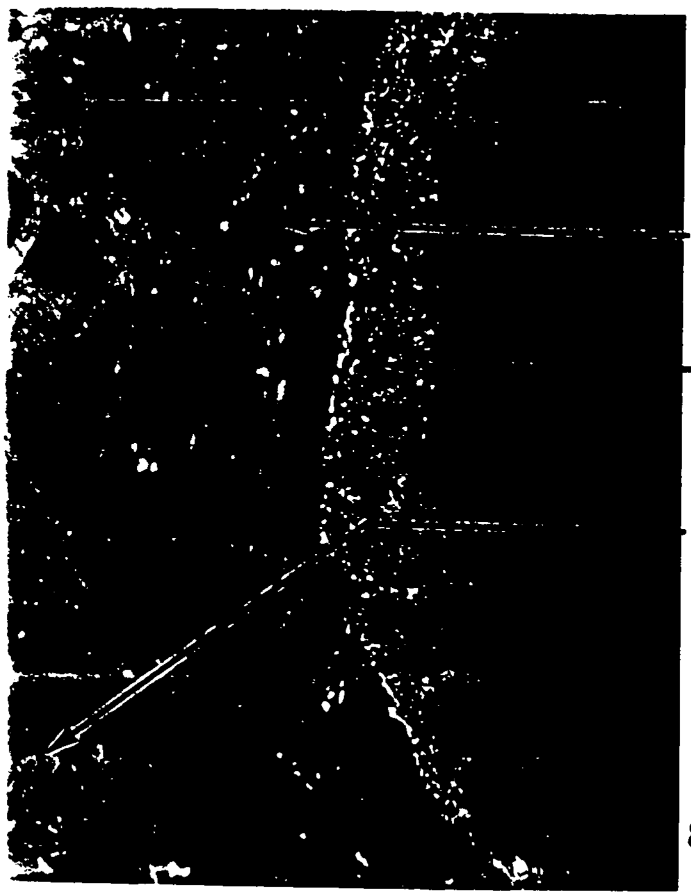


SEM Photomicrograph and X-Ray Elemental Map of Catalyst with 33,679 in-use miles



30X

80X



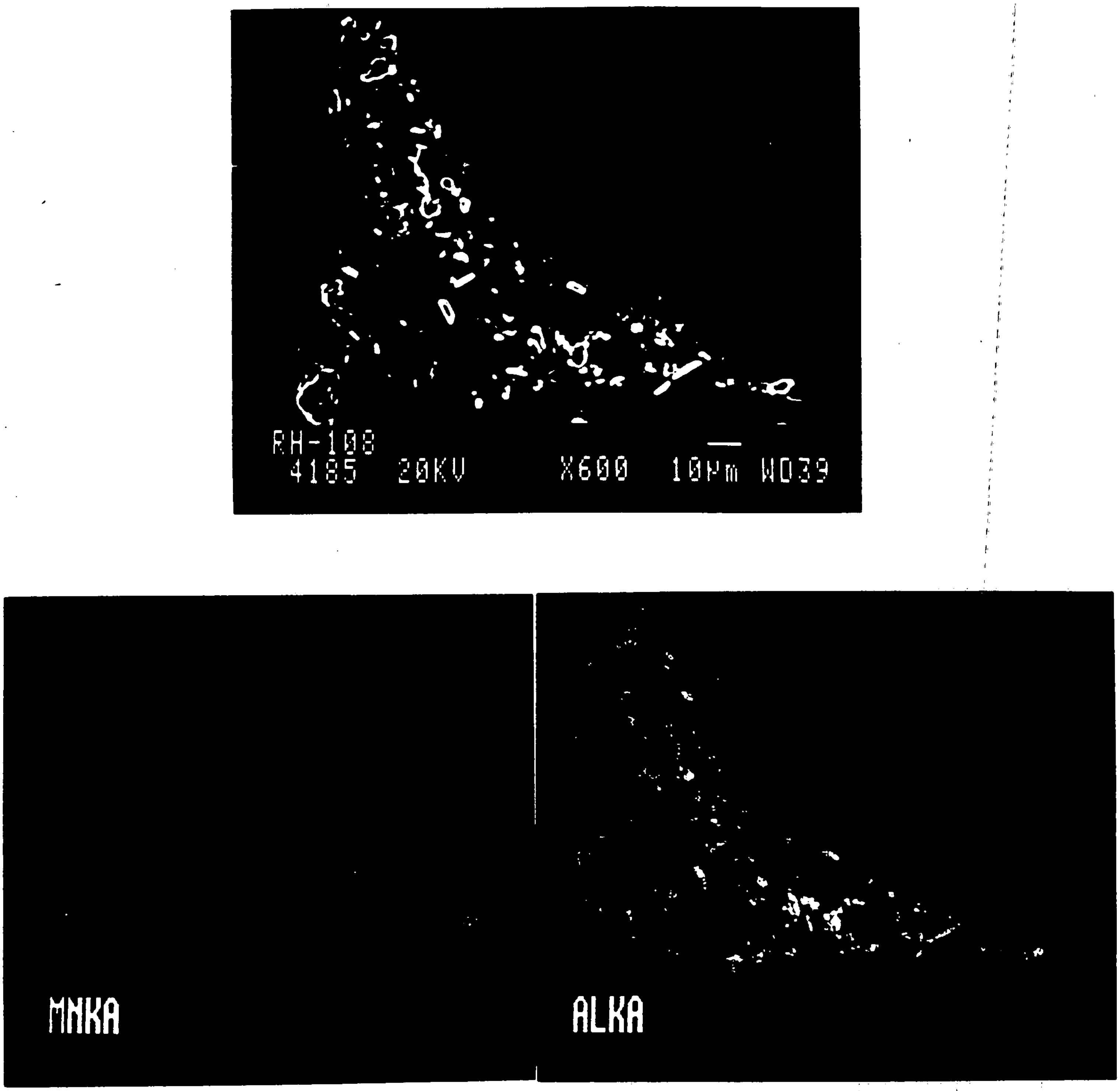
Washcoat

Mn_3O_4 Layer

Substrate

800X

Optical Micrographs of Inlet of Catalyst with 44,740 miles



SEM Photomicrograph and X-Ray Elemental Map of Catalysts
with 44,740 miles

90 16

ATTACHMENT 3

"CHARACTERIZATION OF AUTOMOTIVE CATALYSTS EXPOSED TO THE FUEL ADDITIVE MMT" (SAE 890582)

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890582

Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT

Ronald G. Hurley, William L. H. Watkins
and Robert C. Griffis
Ford Motor Co.

International Congress
and Exposition
Detroit, Michigan
February 27–March 3, 1989

a two brick system and others were a single brick system. On the average these vehicles had accumulated 30,000 in-use miles. Characterizations performed consisted of visual examination, analysis by x-ray fluorescence (XRF), BET surface measurements, optical and scanning electron microscopic (SEM) examination of the washcoat conditions, contamination profiles and catalyst activity. Each of these analytical techniques is a standard post-mortem method for the characterization of in-use catalysts and will not be described in this paper.

Table 1

Vehicle Aged Catalysts Evaluated for Effects of MMT

No.	Engine Type	Model Year	Vehicle Type	Miles	Bricks
301-A	2.8L	1984	Bronco II	43K	2
301-B	2.3L HSC	1986	Topaz	24K	2
301-C	2.3L HSC	1985	Tempo	34K	1
301-D	1.9L 2V	1986	Lynx	22K	2
301-E	1.9L 2V	1985	Escort	28K	2
301-F	2.3L HSC	1984	Topaz	28K	1
301-G	2.3L HSC	1986	Tempo	22K	1
301-H	2.3L EFI	1985	Merkur	32K	2
301-I	2.3L OHC	1984	Ranger	33K	2

The catalysts received for evaluation, as shown in Table 1, were from 1984-1986 vehicles equipped with either 2.3L, 2.8L, or 1.9L engine. Each catalyst was sampled using standard techniques that have been described elsewhere in the literature (2). For x-ray fluorescence (XRF) the catalyst was cored and the resulting core divided into samples of inlet, middle, and outlet for analysis. Each sample consisted of approximately 6 grams of catalyst or sample plus corderite (fresh substrate) to approximate 6 grams. From a core portioned inlet, middle, and outlet a 0.5 gram sample from each was used for the standard BET analysis. Optical and scanning electron microscopic (SEM) samples were also selected in a similar manner as the XRF samples. For this analysis each inlet, middle and outlet sample was mounted and polished to provide a flat surface for analysis. Additional SEM samples were taken by breaking off portions of the catalyst, coating with a thin layer of gold or carbon to provide a conductive surface, and mounting on a carbon block for surface morphological examination. Samples for catalyst activity, steady state R and light-off analysis contained only the first 1/2 inch segment of inlet, middle, and outlet. Instrumentation for the MMT characterization included a SIEMENS SRS 300/VAX x-ray fluorescence spectrometer for XRF analysis. A QuantChrom Quantector Gas Flow System with a Quantasorb Flow Control Accessory was used for BET surface area measurements. The scanning electron microscope used in this characterization was an ETEC Autoscan equipped with a DELTA 3 Kevex energy dispersive x-ray system and a Kevex QUANTUM detector. Optical micrographs were taken using a Reichert metallograph for macros and a Neophote metallographs for micros. Steady state three-way activities and light-off curves were measured in a flow reactor over a range (lean-to-rich) of feed gas compositions.

RESULTS AND DISCUSSIONS

The typical as-received condition of the catalysts used in this study is shown in figure 1. Visually, the interior of the converters have a heavy to moderate coating of a rust colored residual deposit. Further visual inspection show that all of the catalyst cores have light to moderately heavy channel clogging of the inlet core of the first brick. Channel clogging of the catalyst core appears to be consistent and is limited to the first brick of the converter. Only one of the converters shows visual signs of exposure to high operating temperatures. This converter is shown in figure 2.

The results of x-ray fluorescence analysis of samples taken from each catalyst are shown in Table 2. These results summarize the concentration of the contaminants found to be present on the catalysts examined. Manganese concentration, as one might expect, is highest on the inlet of the catalyst and decreases toward the outlet. The Mn concentration range on the first brick, between a low of 1.4 wt% for a vehicle mileage of 24,000 to a high of 6.4 wt% for a vehicle having accumulated 33,000 in-use miles. The x-ray data are consistent with the visual examination in that the highest Mn concentration is limited to the first brick of the converter. The anomaly of Mn concentration reversal (low Mn on the inlet and higher on the outlet) as shown in 301D-1,-2 is due to exposure of this catalyst to high operating temperature which resulted in substantial substrate melting (figure 2). It is important to note that other contaminants S, P, Zn, and Pb, are generally in an acceptable range, somewhat higher than one might expect for this level of accumulated mileage. In addition, one might also expect that the Pb concentration would be higher than normal because of the possibility of the use of fuel from lower quality fuel refineries. This is evident in some of the catalyst but not to an extreme degree. The x-ray results are inconclusive in their tendency to confirm earlier studies that Mn_3O_4 acts as a scavenger (3) in the exhaust for transporting away fuel- and oil-derived catalyst poisons such as Pb, P, and Zn.

X-Ray diffraction analysis of the finely divided, rust colored deposits on the first brick indicates that this residual layer is primarily Mn_3O_4. These results confirm earlier experimental results (3,5) in that Mn derived

890582

Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT

Ronald G. Hurley, William L. H. Watkins
and Robert C. Griffis
Ford Motor Co.

ABSTRACT

A series of in-use catalysts having mileage of 22,000 to 43,000 miles was characterized to determine the effect of the fuel additive MMT. The analytical techniques included visual examination, x-ray fluorescence, x-ray diffraction, optical microscopy, scanning electron microscopy, and electron microprobe. In addition, catalyst activity was measured and compared to the catalyst activity from a pulsator aged catalyst without the MMT additive in the feed gas composition. Characterization results show a significantly thick layer (5-20 microns) covering the surface of the catalysts which results in the increase of mass transfer resistance. Steady state R and light-off measurements indicated catalyst efficiency is also significantly reduced as exposure to MMT is increased.

In September, 1978 the addition of methylcyclopentadienyl manganese tricarbonyl (MMT) to gasoline fuel was denied by EPA. This denial was based on the failure to establish that the additive MMT would not cause or contribute to the failure of any 1975 or later model year vehicle to comply with applicable emission standards. In the meantime considerable experience has been accumulated in Canada where MMT at a concentration of 16.5 mg/l (1/16 g/gal) is added to fuel as an octane improver. The supplier of the octane improver, MMT, claims to have received no complaints regarding engine or exhaust system performance in approximately 400 billion in-use miles.

Considerable research has been done since the 1978 ruling on the use of MMT as a fuel additive (1-5). Wallace, et al. (5) and Benson, et al. (1) have shown that with 88% to 99% confidence that MMT adversely affects light duty vehicle tail pipe HC emissions at the MMT concentration 16.5mg/gal. Conversely, MMT did not statistically show a consistent adverse effect on CO or NO_x exhaust emission. Hughmark, et al. (4) conclude that MMT actually increases converter efficiency in relation to clear fuel. Williamson, et al. (2) concluded that the "catalyst enhancement phenomena" which resulted in the 2-3% HC improvement in catalyst efficiencies in the CRC study as well as the apparent beneficial effects observed in his research can perhaps be attributed to the scavenging effect or to catalytic activity of the MMT combustion product, Mn_3O_4(3). However, in each case the author examined the effects of MMT on emissions and did not particularly focus on the effects on the catalyst or determine the possible mechanism of catalyst deactivation. Consequently, and in response to the possibility of the EPA granting a waiver of the 1978 ruling and the subsequent use of an MMT additive in US gasoline, a study was undertaken to characterize, examine and evaluate a series of catalysts removed from in-use vehicles. The major objective of this paper, therefore, is to present an evaluation and characterization of the long term durability and efficiency of catalysts exposed to the fuel additive MMT.

EXPERIMENTAL

Nine (9) catalysts (Table 1) that had been exposed to MMT were removed from vehicles under warranty because of suspected converter defects. It should also be noted that these catalysts were taken from vehicles in which the authors had no means of verifying their fueling characteristics nor their proper function. Therefore, it was assumed by the authors that the vehicles used for this study were properly adjusted and fueled with gasoline that met the Canadian standard of 1/16 g/gal of MMT. As shown in Table 1 some of these converters were

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Table 2

CONTAMINANT ANALYSIS OF AUTOMOTIVE CATALYSTS EXPOSED TO MMT

Vehicle Catalyst		Miles	Type	Contaminants, Wt% Mn	S	P	Zn	Pb
301A-1	I	43,000	TWC	2.08	0.0	.46	.14	.67
	M			.83	0.0	.16	.05	.04
	O			.53	0.0	.10	.03	.07
301A-2	I		COC	.83	0.0	.16	.06	.21
	M			.28	0.0	.06	.02	.12
	O			.26	0.0	.05	.01	.12
301B-1	I	24,000	TWC	1.43	.14	.13	.12	.07
	M			.37	.12	.06	.03	.03
	O			.35	.12	.06	.02	.06
301B-2	I		COC	.48	.21	.08	.02	.04
	M			.19	.20	.04	.01	.02
	O			.16	.16	.04	.01	.01
301C	I	34,000	TWC	5.20	.14	.39	.28	.41
	M			2.57	.05	.25	.13	.22
	O			2.24	.03	.23	.10	.21
301D-1	I	22,000	TWC	.79	.0	.07	.02	.03
	M			.80	.0	.06	.01	.02
	O			2.18	.01	.18	.09	.19
301D-2	I		COC	1.62	.16	.11	.01	.07
	M			.69	.02	.06	.01	.23
	O			.60	.06	.06	.02	.13
301E-1	I	28,000	TWC	1.77	.05	.18	.08	.54
	M			.91	.05	.09	.02	.02
	O			1.08	.08	.09	.02	.02
301E-2	I		COC	1.76	.12	.13	.04	.30
	M			.86	.10	.08	.01	.34
	O			.77	.11	.07	.01	.49
301F	I	28,000	TWC	3.15	.11	.22	.20	.74
	M			2.14	.06	.11	.11	.46
	O			1.76	.05	.10	.08	.37
301G	I	22,000	TWC	4.20	.26	.27	.24	.22
	M			2.05	.11	.19	.13	.09
	O			1.58	.14	.15	.09	.06
301H-1	I	32,000	TWC	1.72	.12	.24	.25	.02
	M			.92	.13	.12	.11	.03
	O			.75	.12	.10	.07	.03
301H-2	I		COC	.81	.12	.11	.08	.04
	M			.51	.13	.06	.04	.03
	O			.41	.14	.06	.03	.03
301I-1	I	33,000	TWC	6.14	.02	.63	.58	.52
	M			2.70	.0	.29	.13	.14
	O			1.98	.0	.25	.11	.08
301I-2	I		COC	3.39	.0	.37	.28	.33
	M			1.71	.0	.18	.06	.09
	O			1.49	.0	.16	.04	.11

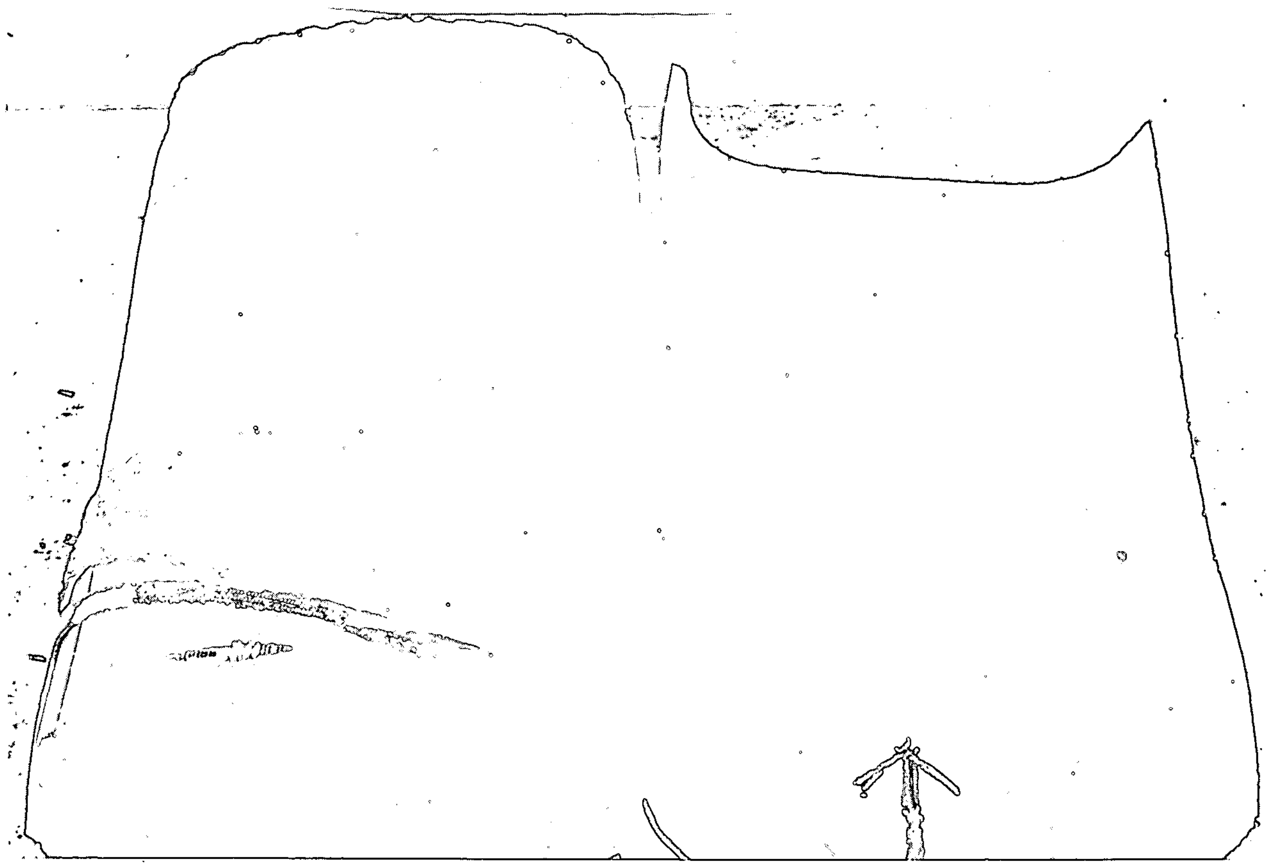

Figure 1. Example of the as-received condition of the in-use converters.

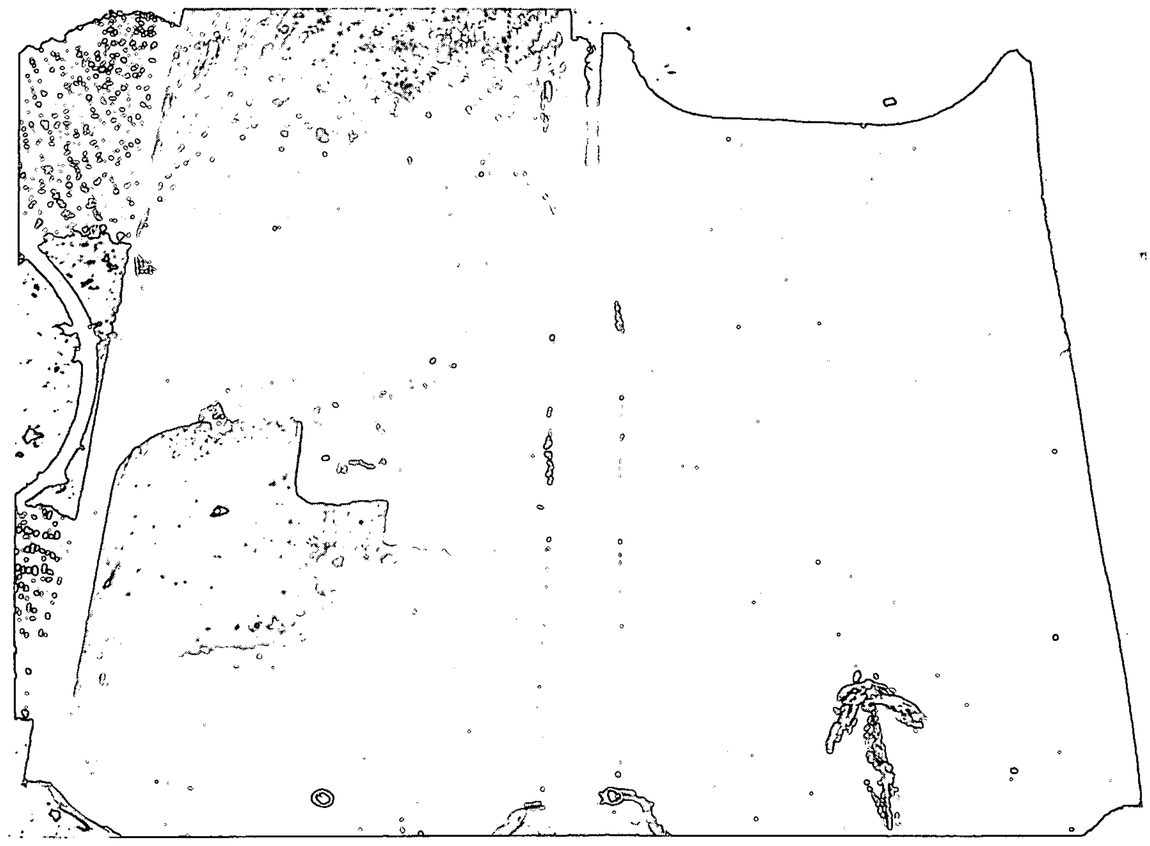

Figure 2. Example of in-use converter showing exposure to high operating temperature in the as-received condition.

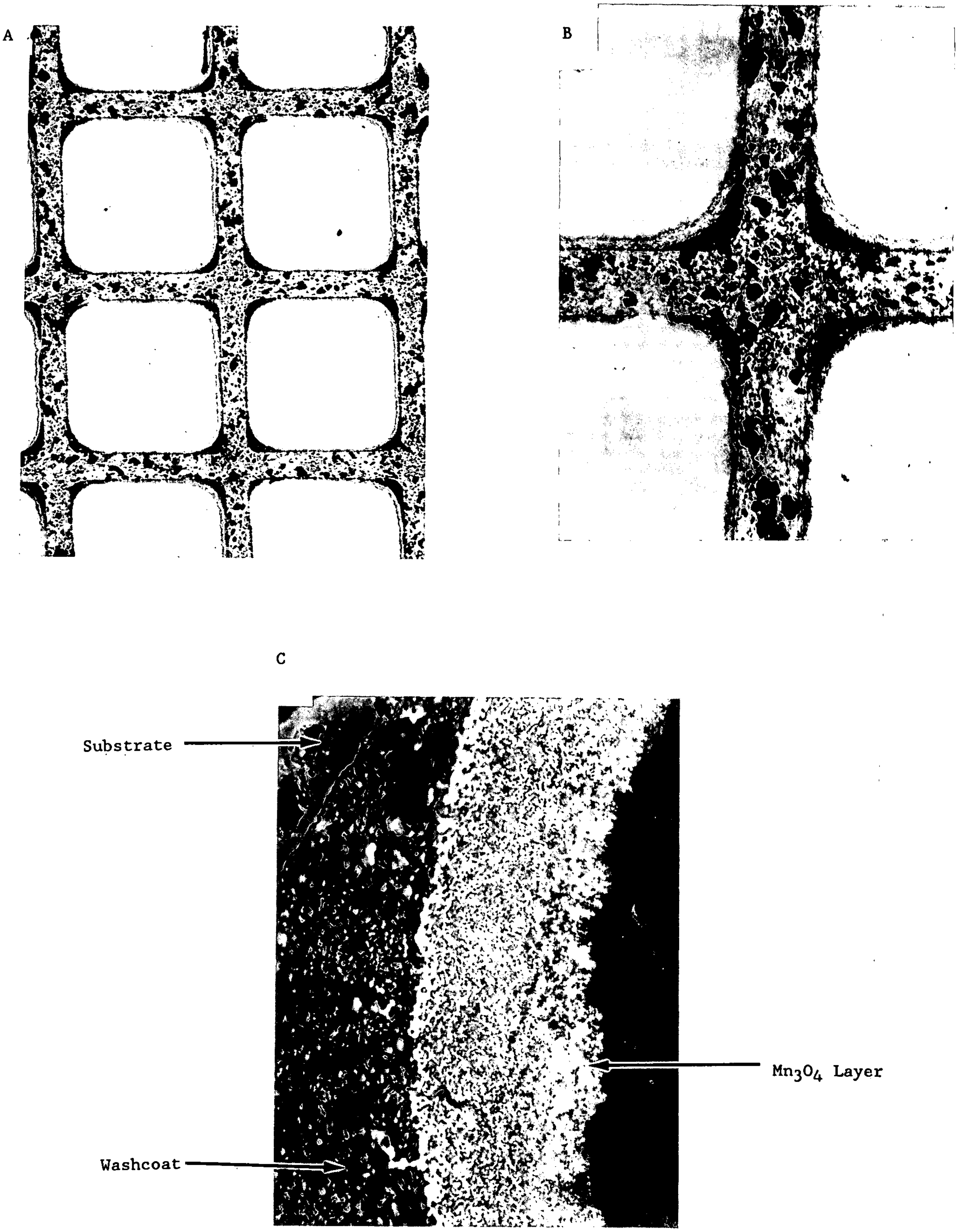

Figure 3. Optical Micrographs of 33,000 mile MMT exposed catalyst TC-301I at (a) 30X, (b) 80X, and (c) 800X.

from MMT is converted in the combustion process exclusively to Mn_3O_4.

Optical micrographs (figures 3 and 4) of catalysts, 301G and 301I, show a heavy residual layer covering the washcoat. X-Ray fluorescence results indicate that these two samples, contain approximately 4 and 6 wt% of Mn, respectively and are from vehicles with 22,000 and 33,000 accumulated in-use miles. As is evident in both of the high magnification micrographs, from 301G and 301I, the Mn_3O_4 is on layered on the surface of the washcoat. It does not appear to penetrate or have reacted with the washcoat but simply adheres to the surface. This deposit of Mn_3O_4 on the washcoat may cause physical pore plugging and thus result in mass-transfer problems.

Scanning Electron Microscopic and Electron Probe analysis show the thickness of the Mn_3O_4 residual layer to range from approximately 5 microns to a maximum of approximately 20 microns. The thickest layer is observed on catalyst 301I which had 33,000 accumulated miles. SEM micrographs (figure 5) of cross-sections of 301G and 301I show this layer quite distinctly. Also shown in this figure is a Mn x-ray elemental map pattern to confirm that the layer is indeed rich in Mn. This elemental map is used to determine the actual thickness of the Mn rich region on the washcoat. This micrographs also indicate little if any penetration into the washcoat by the Mn rich layer. Indications from the surface morphology study is that the Mn rich layer does simply adhere to the surface of the washcoat. An example of the surface morphology of the Mn rich layer is shown in figure 6. As is shown in the micrograph the surface is covered with a layer of fluffy, porous material. This material was confirmed by XRD to consist exclusively of Mn_3O_4.

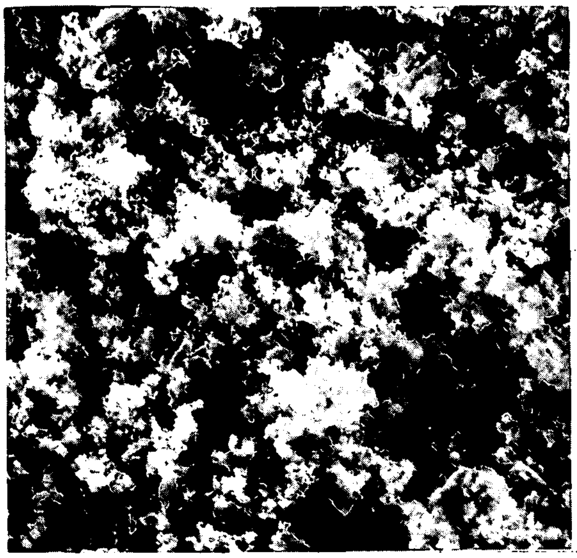

Figure 6. Surface morphology of Mn rich layer on 33,000 mile MMT exposed catalyst.

BET surface areas (Table 3) range between 14.0 m^2/gm and 0.9 m^2/gm for the first brick and between 9.3 m^2/gm and 0.6 m^2/gm for the second brick. In general, as shown in Table 3, all the surface area measurements were lower than that of a fresh catalyst's surface area of approximately 25 m^2/gm. The lower BET values measured for the catalysts could be due to two mechanisms: 1) exposure to higher than normal operational temperatures and 2) the reduction of active surface area sites by the heavy coating of Mn_3O_4. However, there is no prior experimental evidence that the combustion products of MMT reduces "active surface area sites". Most likely the Mn_3O_4 deposits cause pore plugging and subsequent mass transfer problems. This diffusion hinderance would certainly be reflected in a erroneous decrease of the BET areas, if measured by one-point dynamic desorption.

Conversion efficiencies were measured for two of the MMT exposed catalysts, 301G and 301I having accumulated 22,000 and 33,000 miles, respectively. In addition, a comparison of the catalyst efficiency was made between a pulsator aged catalyst and the MMT exposed catalysts. The pulsator aged catalyst was aged with a "low-lead" (no MMT) simulated certification fuel, i.e., isooctane containing 2 mg Pb + 0.8 mg P + 0.03 wt % S/gal, to the equivalent of 15,000 miles. The activity and three-way selectivity of catalysts is expressed as percent conversion of NO, CO, and HC against the redox ratio (R) of the reacting gas mixture. These points are plotted over a range of rich to lean air fuel ratio to obtain an R curve. Optimum selectivity and redox ratio values corresponding to the peak three-way conversion point are determined by interpolation from resulting curves. As shown in equation below, R is obtained by dividing the sum of the equivalent reducing components of the mixture by the sum of the oxidizing components. Thus

$$R = \frac{pCO + pH_2 + 3nC_nH_2n + 3.33npC_nH_{2n} + 2}{pNO + 2pO_2}$$

Therefore a value of $R > 1$ represents an overall reducing gas mixture and a value of $R = 1$ represents a stoichiometric gas mixture. The redox ratio, a measure of the exhaust stoichiometry and related to the A/F ratio, is a measure of the fuel mixture stoichiometry. It is a more sensitive yardstick, since, in the exhaust, most of the mixture has been burned away. Steady-state R curves (measure of catalyst conversion efficiency with respect to HC, NO, and CO) and light-off temperatures were measured on a flow reactor over a range (lean-to-rich) of feed gas composition. A comparison of steady-state R curve data (figure 7) between the MMT exposed and a non-MMT exposed catalyst indicate equal deterioration among the three catalysts for CO activity. However, there was

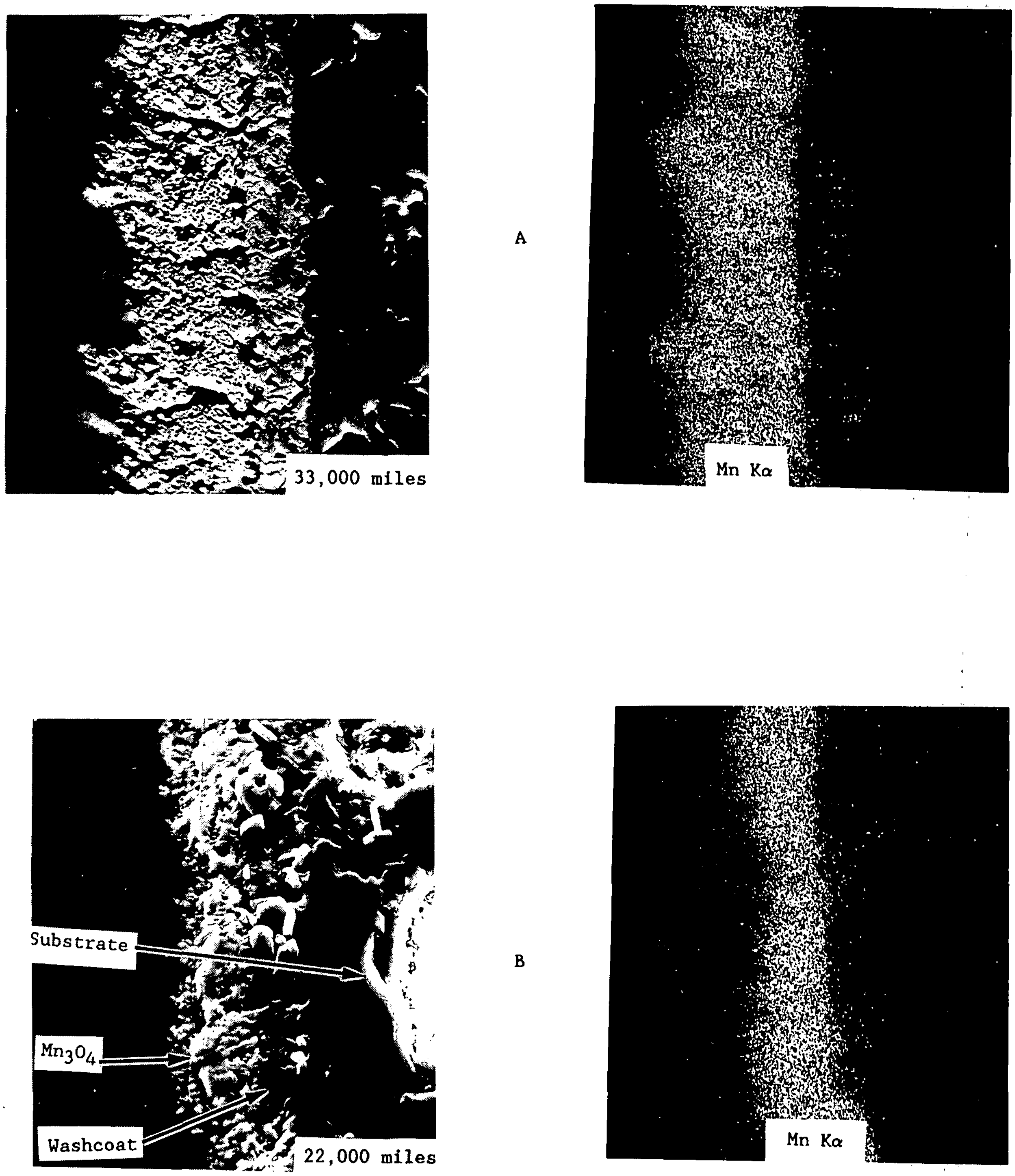

Figure 5. Scanning electron micrographs and Mn Kα elemental maps of (a) 33,000 miles MMT exposed catalyst and (b) 22,000 miles MMT exposed catalyst. (1 cm = 10 microns).

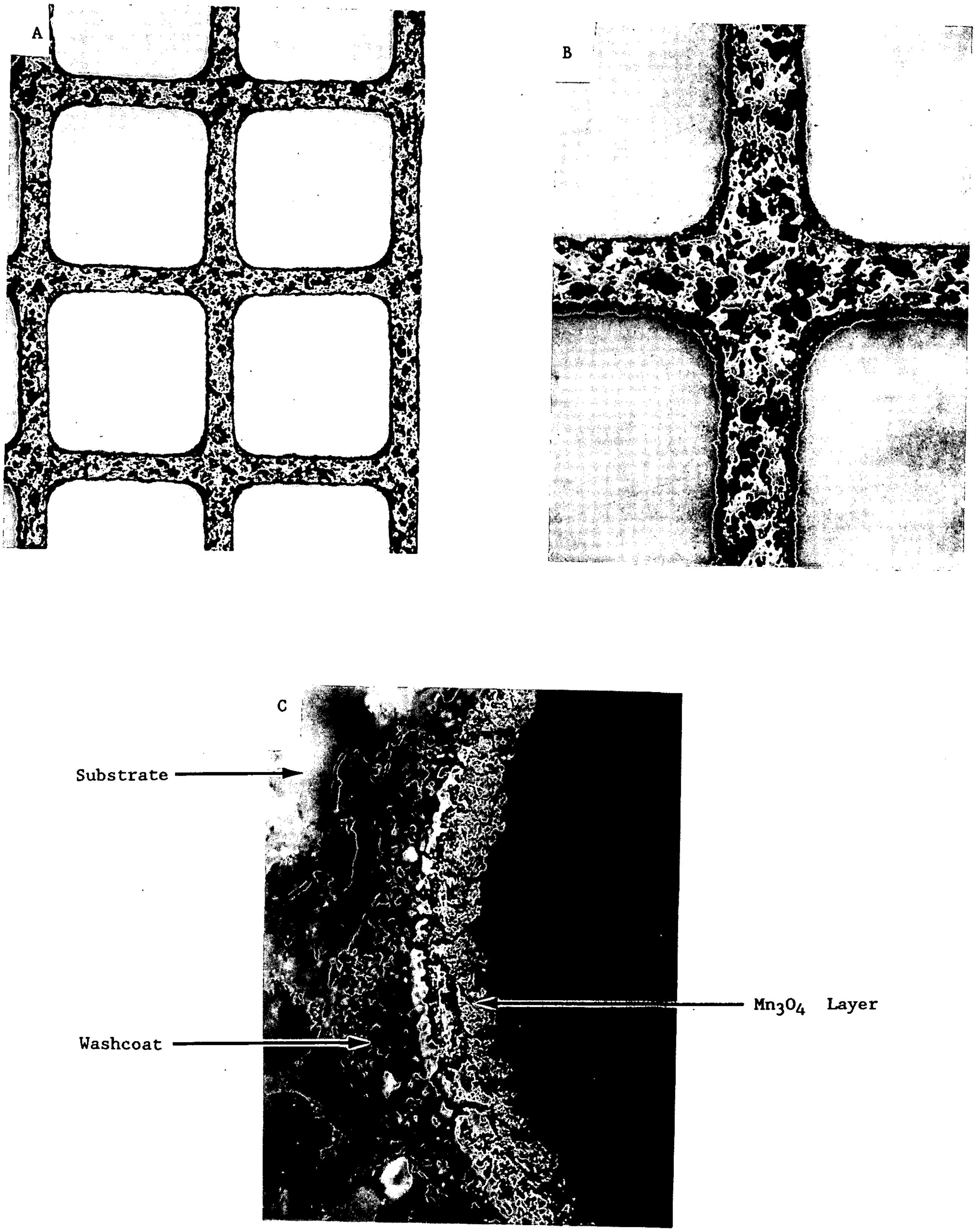

Figure 4. Optical micrographs of 22,000 mile MMT exposed catalyst TC-301G at (a) 30X, (b) 80X, and (c) 800X.

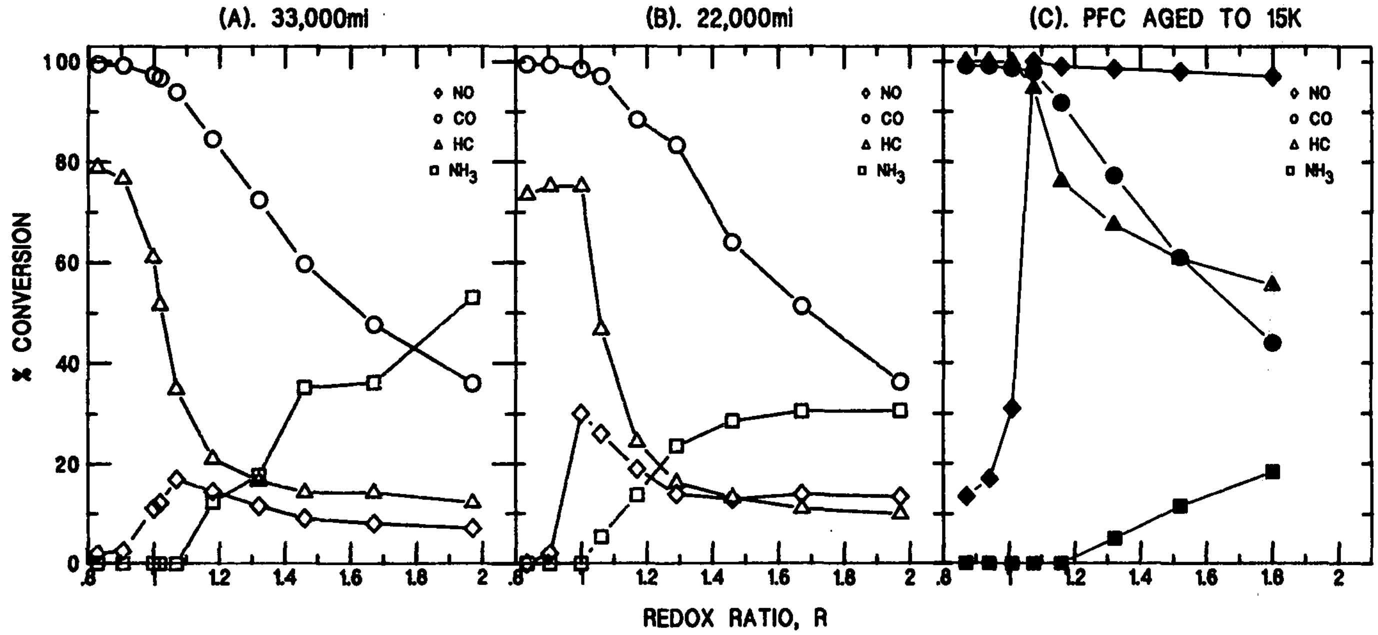

Figure 7. Comparison of the steady-state NO, CO, and HC activities for (a) 33,000 miles MMT exposed catalyst, (b) 22,000 miles MMT exposed catalyst, and (c) 15,000 mile non-MMT pulsator aged catalyst.

extreme deterioration of NO and HC activity for the MMT exposed catalysts. The peak NO conversion as measured at an R value of 1.07 was 100%, 27%, and 15% for the pulsator aged catalyst and the MMT catalysts 301G, 301I, respectively. The peak HC conversion at an R value of 1.07 was measured to be 95%, 43%, and 32% for the pulsator aged catalyst and the MMT catalysts 301G, 301I, respectively. In addition, the data indicate that NH_3 formation increases as the catalyst is exposed to MMT. This is understandable because Mn_3O_4 is not a selective catalyst to reduce NO to N_2.

A comparison of steady-state light-off curve data (figure 8) between the MMT exposed and a non-MMT exposed catalyst show 80% conversion for HC, CO, and NO for the pulsator (non-MMT) catalyst to be at approximately 280° C. Whereas 80% conversion for CO was approximately 410° C for catalyst 301G and approximately 460° C for catalyst 301I. Eighty (80) percent conversion does not take place for HC or NO for either MMT exposed catalyst. The curves also show that 50% conversion of HC, CO, and NO takes place at approximately 250° C for the pulsator aged catalyst. Fifty (50) percent conversion for CO and HC takes place at 350° C and 460° C, respectively, for catalyst 301G. Likewise, 50% conversion of CO and HC takes place at 400° C and 530° C, respectively, for catalyst 301I. The data indicate that 50% conversion does not take place for NO on either of the MMT exposed catalyst.

CONCLUSIONS

Although the authors had no means of verifying the fueling characteristics of the vehicles nor the proper function of the vehicles from which the catalysts were taken, the conclusions are based on the assumption that these vehicles were properly adjusted and fueled with gasoline containing 1/16 g/gal MMT. The following salient results obtained from the post-mortem analysis of these catalysts can be summarized as follows:

- Minor to severe clogging of the first brick by the residue of the oxidation product of MMT, Mn_3O_4,
- 5-20 micron thick layer of Mn_3O_4 over the washcoat surface,
- decrease in surface area (BET) measurements,
- percent conversion of NO, CO, and HC decreases as the exposure to MMT increases,
- NH_3 formation increases as the exposure to MMT increases, and,
- light-off temperatures for NO, CO, and HC increase as the exposure to MMT increases.

The mechanism of deactivation as determined by this analysis is due to the clogging of the

Table 3

B.E.T. SURFACE AREA MEASUREMENT OF AUTOMOTIVE CATALYSTS EXPOSED TO MMT

Vehicle Catalysts		Type	Miles	B.E.T. Area (M^2/g)
301A-1	I	TWC	43,000	3.8
	M			6.8
	O			4.5
301A-2	I	COC		2.7
	M			4.1
	O			4.0
301B-1	I	TWC	24,000	13.9
	M			15.4
	O			12.8
301B-2	I	COC		7.6
	M			8.7
	O			8.2
301C	I	TWC	34,000	8.5
	M			7.4
	O			7.0
301D-1	I	TWC	22,000	.8
	M			.5
	O			1.3
301D-2	I	COC		.3
	M			.7
	O			4.0
301E-1	I	TWC	28,000	4.4
	M			5.6
	O			5.5
301E-2	I	COC		6.9
	M			7.9
	O			8.6
301F	I	TWC	28,000	14.1
	M			12.4
	O			11.0
301G	I	TWC	22,000	7.3
	M			6.7
	O			6.6
301H-1	I	TWC	32,000	8.9
	M			9.8
	O			9.8
301H-2	I	COC		8.4
	M			10.2
	O			9.3
301I-1	I	TWC	33,000	3.8
	M			4.0
	O			4.3
301I-2	I	COC		1.2
	M			0.4
	O			0.3

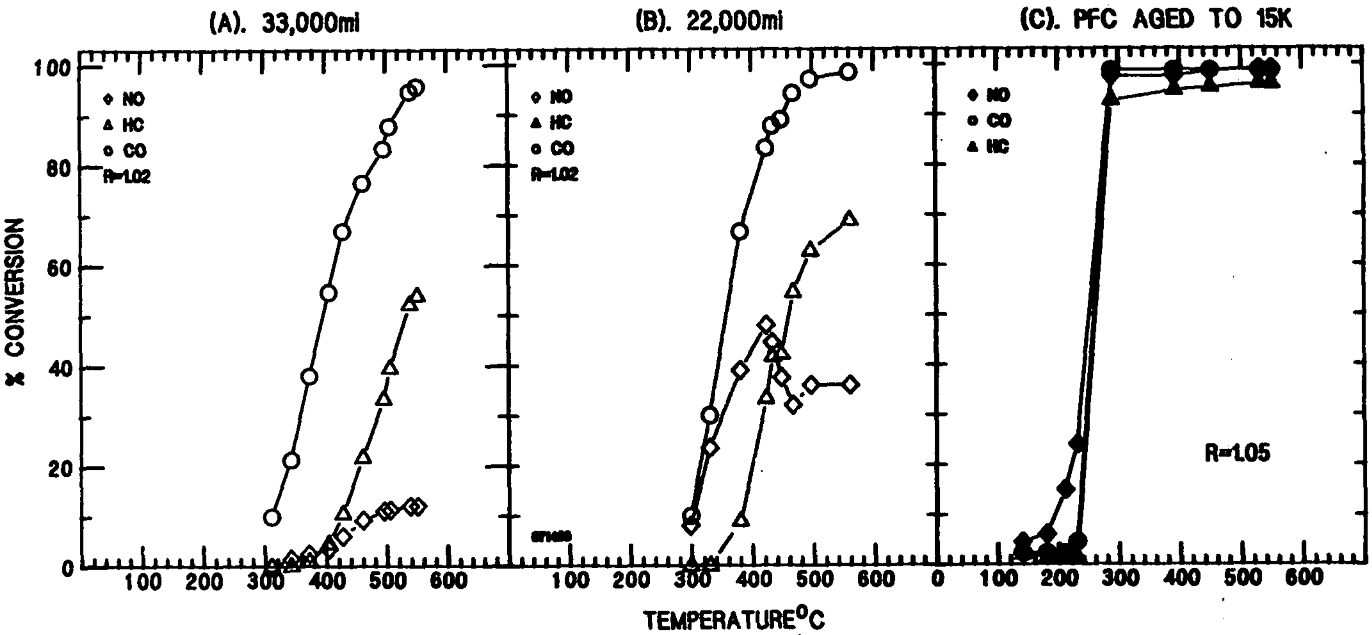

Figure 8. Comparison of the light-off NO, CO, and HC activities for (a) 33,000 miles MMT exposed catalyst, (b) 22,000 miles MMT exposed catalyst, and (c) 15,000 mile non-MMT pulsator aged catalyst.

channels of the converter. This plugging of the channels of the monolith results in an increase of the mass transfer resistance and consequently reduces the efficiency of the catalyst to convert HC, CO and NO_x. Based on these results it appears that the fuel additive MMT had a deleterious effect on the efficiency of the catalysts tested. However, in order to access more definitively the effect of MMT on in-use vehicle catalyst efficiency, this study suggests the need to correlate cause and effect from vehicles fueled with and without the fuel additive MMT.

ACKNOWLEDGEMENTS

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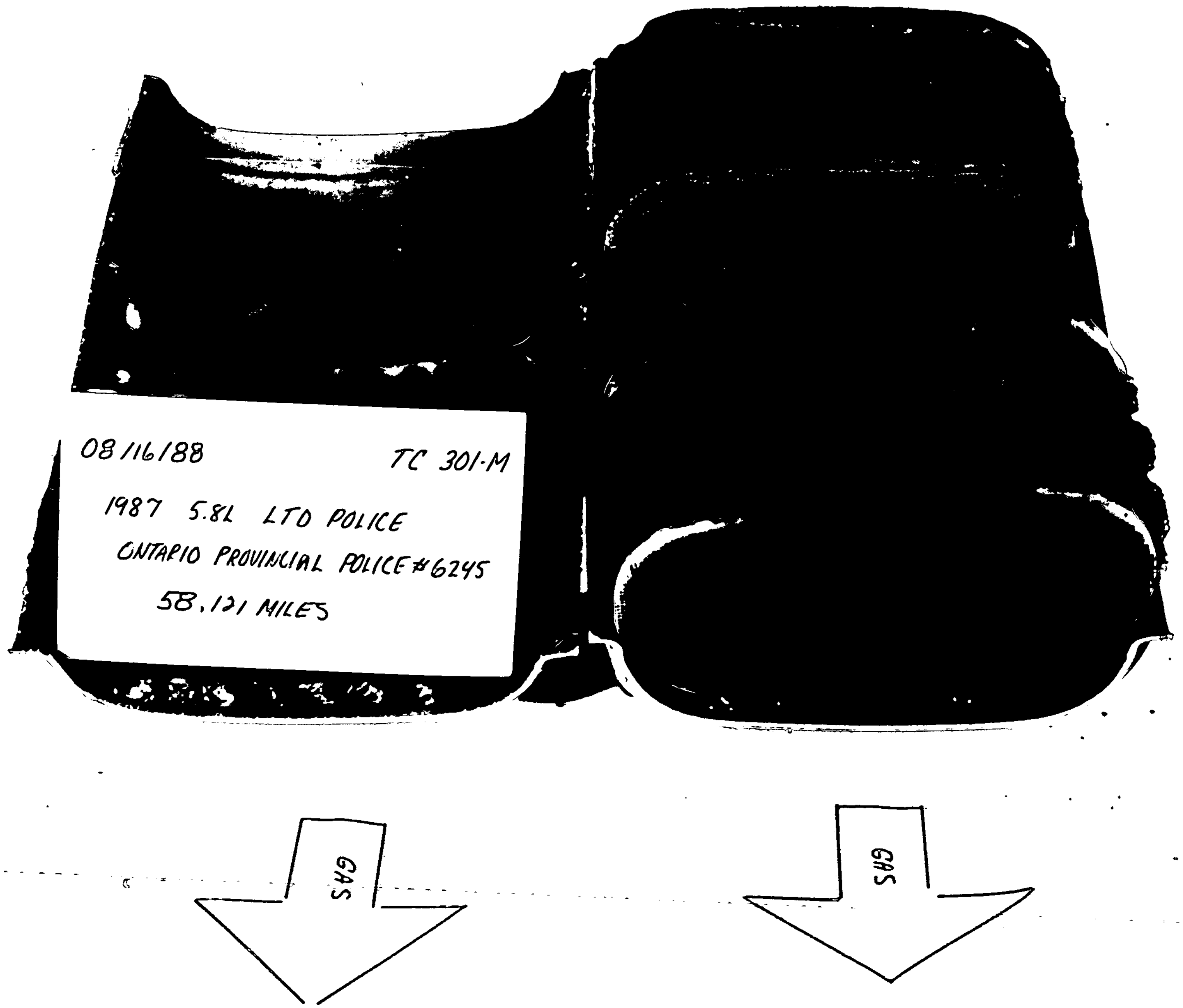
ATTACHMENT 3

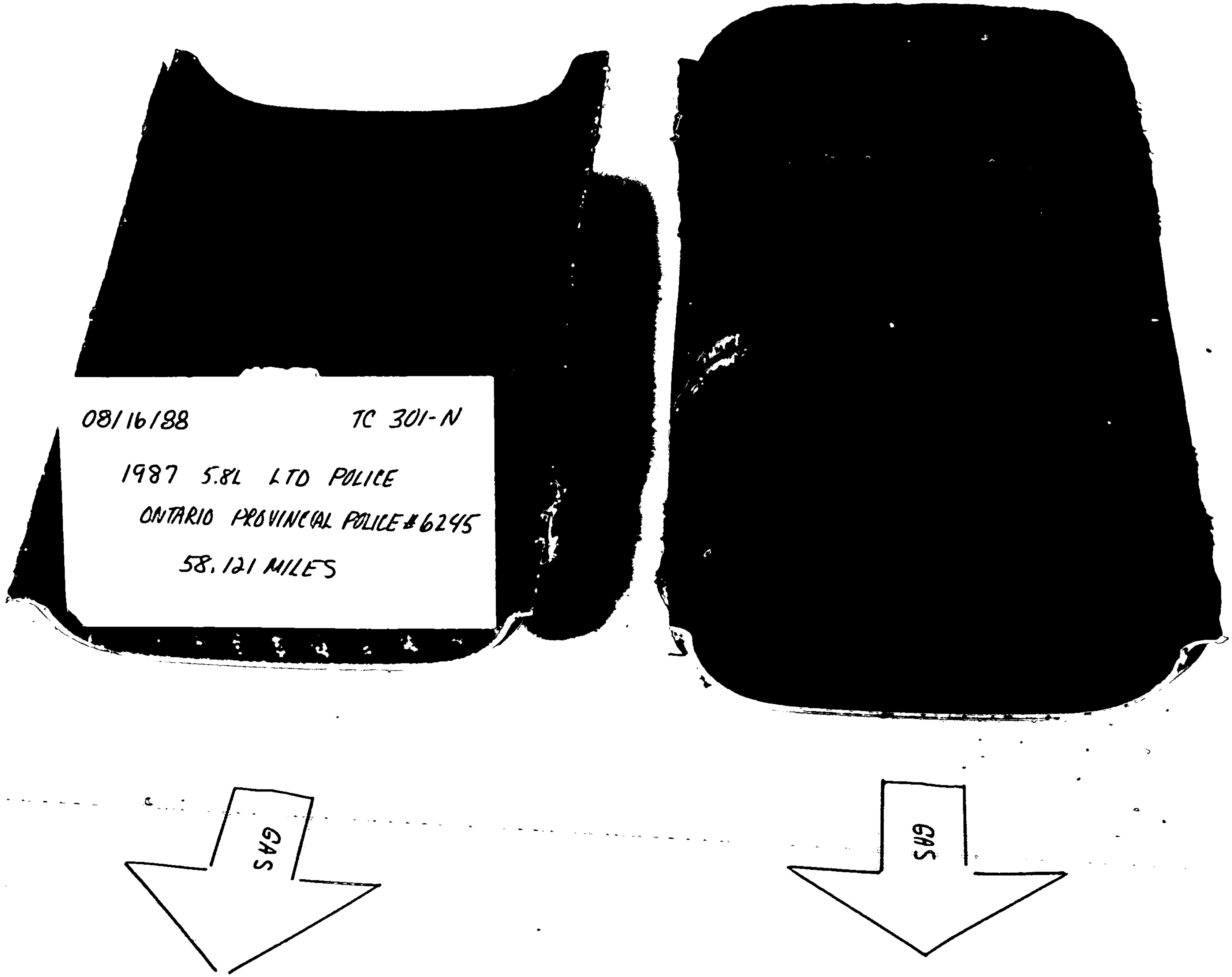
"CHARACTERIZATION OF AUTOMOTIVE CATALYSTS EXPOSED TO THE FUEL ADDITIVE MMT" (SAE 890582)

EFFECT of MMT on Catalysts

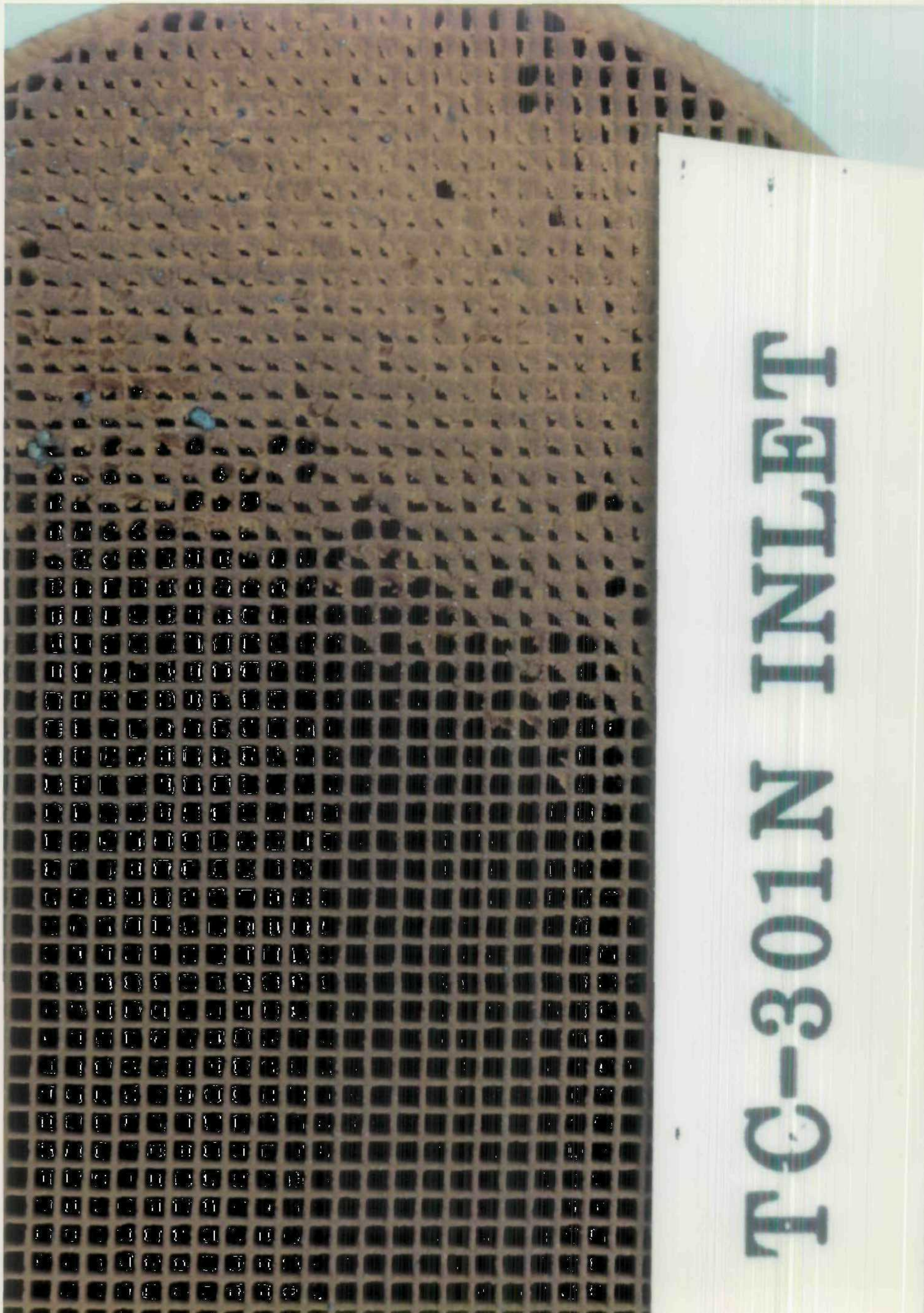
Wt% Mn	Wt% Pb	B.E.T
• 5.63	0.07	4.78
0.92		
0.60		
• 2.12	0.15	12.15
1.14		
0.87		
• 5.06	0.06	5.46
1.05		
0.82		
• 2.25	0.13	10.99
1.42		
1.13		

Note: Ontario Provencial Police Vehicles


08/16/88
TC 301-M
1987 5.8L LTD POLICE
ONTARIO PROVINCIAL POLICE #6245
58,121 MILES
GAS
GAS

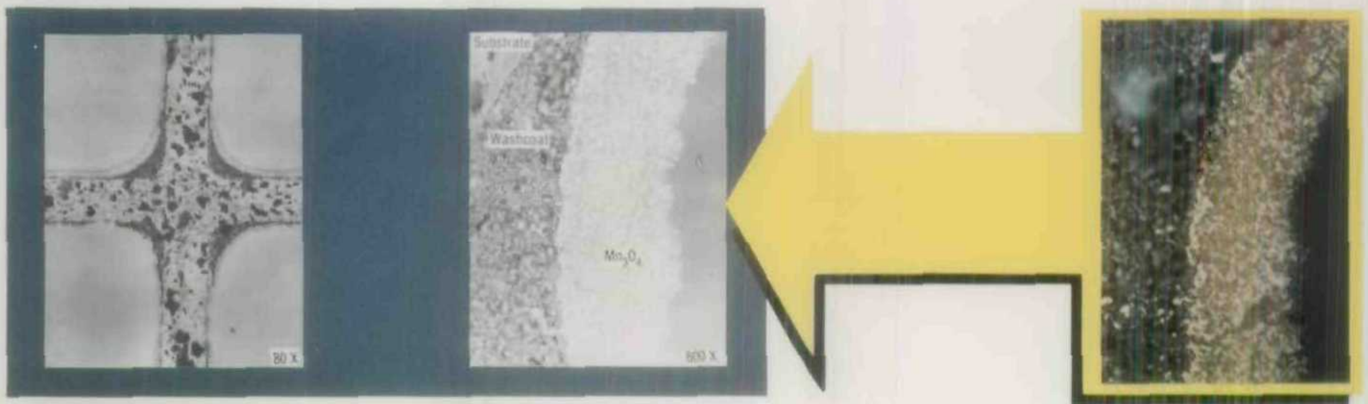

08/16/88
TC 301-N
1987 5.8L LTD POLICE
ONTARIO PROVINCIAL POLICE #6245
58,121 MILES
GAS
GAS


TC-301M INLET

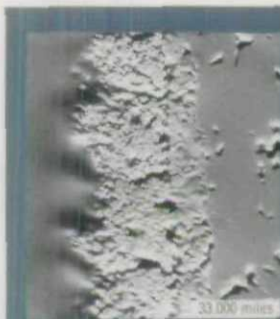

TC-301N INLET

Effect Of MMT On Catalyst

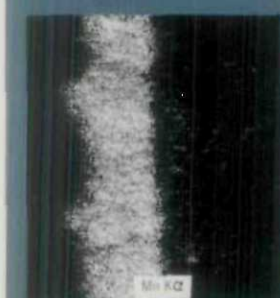
Optical and SEM



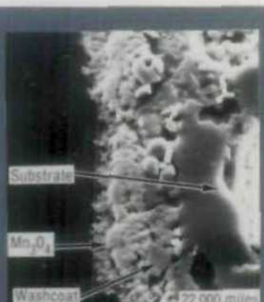
Optical
Micrograph
Of Catalyst
(33,000 miles)



SEM
Micrographs —
Cross-section
Of Catalyst
(1 cm = 10 microns)

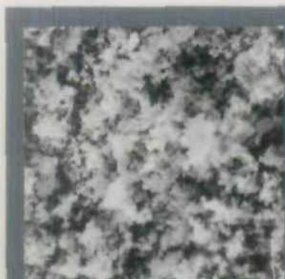


Mn
Elemental Map —
Cross-section
Of Catalyst
(1 cm = 10 microns)



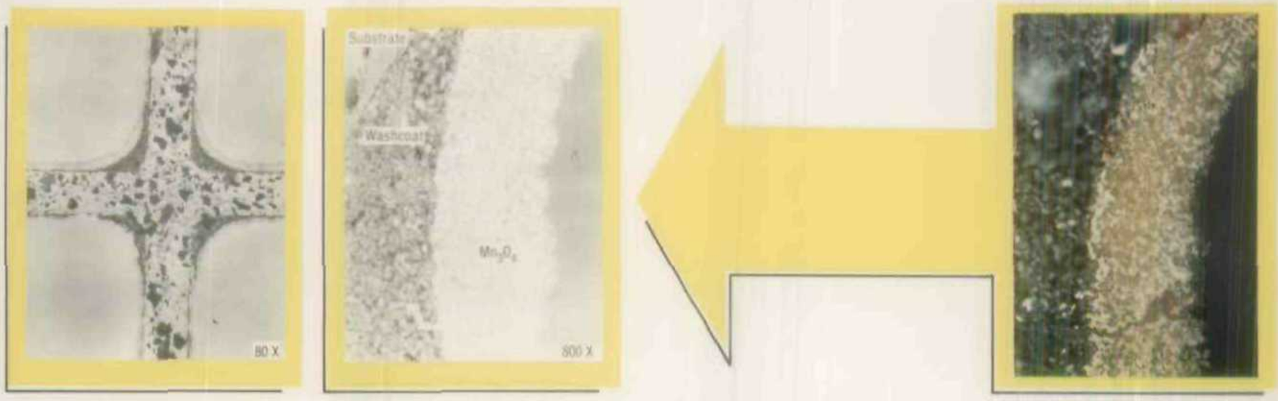
SEM
Micrographs —
Cross-section
Of Catalyst
(1 cm = 10 microns)

Mn
Elemental Map —
Cross-section
Of Catalyst
(1 cm = 10 microns)



SEM
Photomicrograph
Of Surface Morphology
At 33,000 In-use Miles
(1000 X)

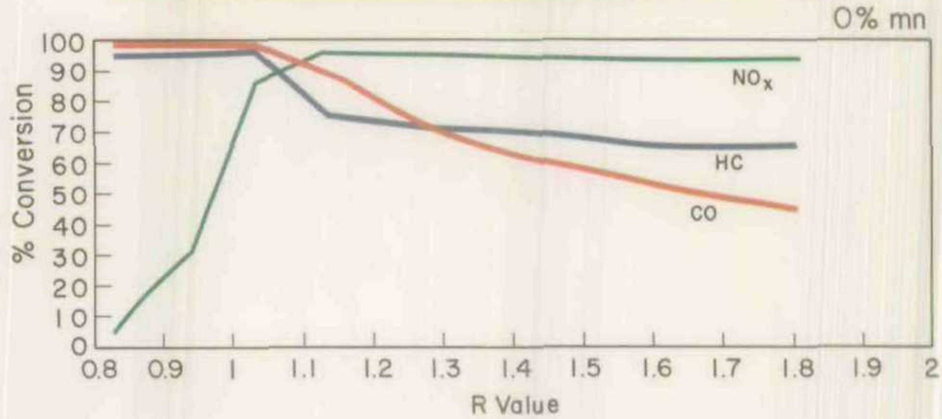
Effect Of MMT On Catalyst



Optical Micrograph of Catalyst (33.000 miles)

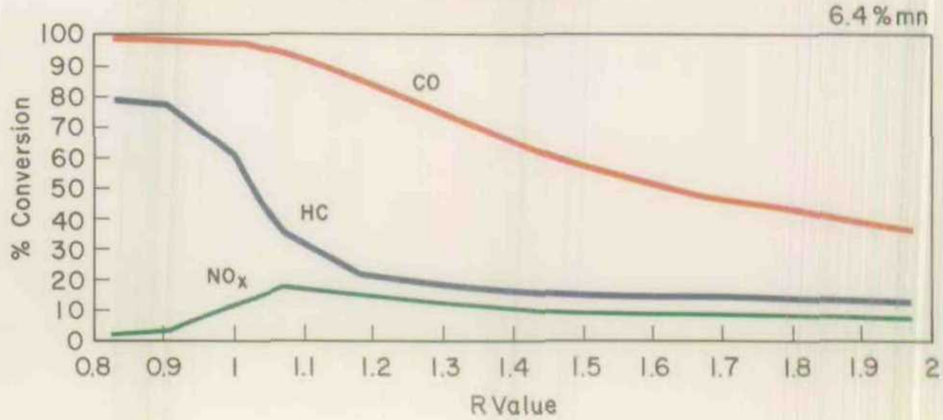
Catalyst Activity - Non MMT Fueled

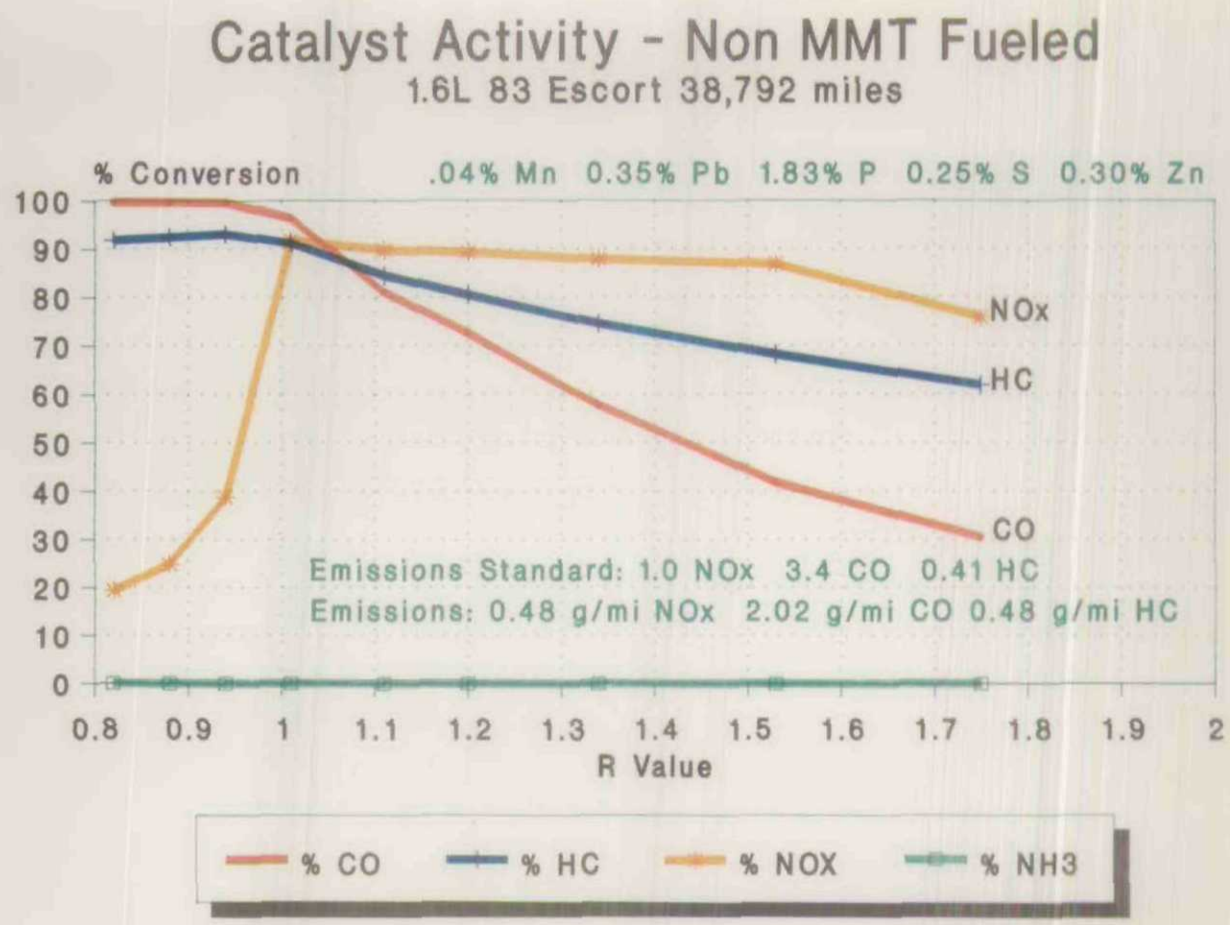
3.0 L 86 Taurus 46,000 Miles

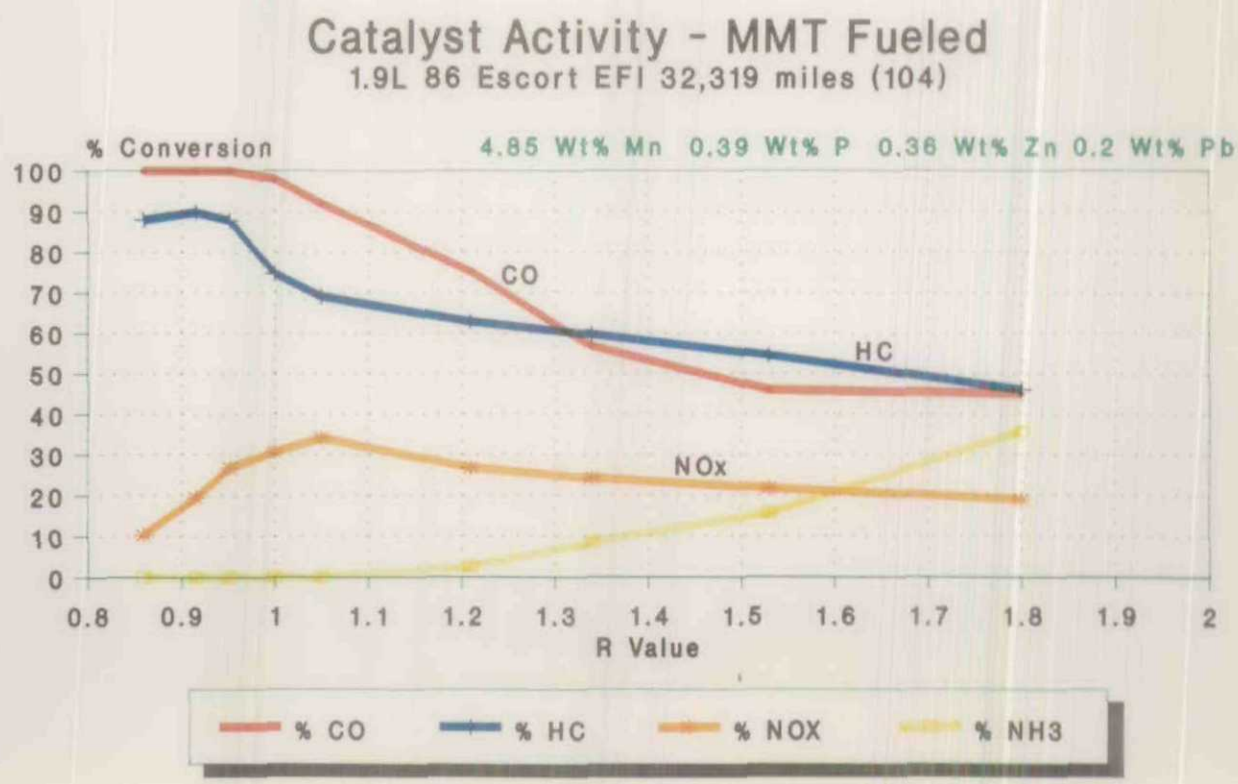


Catalyst Activity - MMT Fueled

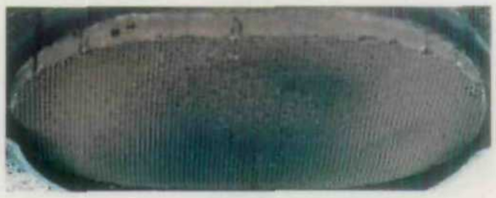
2.3 L Ranger - 33,000 Miles




Catalyst Activity - Non MMT Fueled
1.6L 83 Escort 38,792 miles
% Conversion
.04% Mn 0.35% Pb 1.83% P 0.25% S 0.30% Zn
NOx
HC
CO
Emissions Standard: 1.0 NOx 3.4 CO 0.41 HC
Emissions: 0.48 g/mi NOx 2.02 g/mi CO 0.48 g/mi HC
R Value
% CO
% HC
% NOX
% NH3


Catalyst Activity - MMT Fueled
1.9L 86 Escort EFI 32,319 miles (104)
% Conversion
4.85 Wt% Mn 0.39 Wt% P 0.36 Wt% Zn 0.2 Wt% Pb
CO
HC
NOx
R Value
% CO
% HC
% NOX
% NH3

Effects Of MMT On Catalysts



1986 2.3L Topaz
23,744 Miles
1.4% Mn

1984 2.3L Ranger
32,879 Miles
6.1% Mn

1984 2.3L Ranger
32,879 Miles
6.1% Mn

1985 2.3L Merkur
32,088 Miles
1.7% Mn

1987 5.8L LTD
(Police)
58,000 Miles
5.1 % Mn

Effects Of MMT On Catalysts

- Minor to severe clogging on inlet of catalysts from vehicles operated on MMT laden fuel

- Residue on inlets of catalysts confirmed to be Mn_3O_4 , a combustion product of MMT

- Manganese concentration on inlets of first brick varies between 1.5% and 6.5% for vehicles having between 13,000 and 45,000 miles using MMT laden fuel

- The thickness of the Mn_3O_4 layer on the washcoat varies between 5 and 30 microns for vehicles having between 13,000 and 45,000 miles using MMT laden fuel

- Catalysts efficiency for HC, CO, NO_x emissions is reduced between 50 and 80% by the Mn_3O_4 layer

Effects Of MMT On Catalysts

Summary :

- Catalyst efficiency deteriorates as exposure to MMT increases
- Mechanism of deactivation due to mass transfer resistance caused by Mn_3O_4 buildup on washcoat surface
- Reported on effects of MMT at 1989 International SAE Congress (SAE 890582)
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Analysis Results of 41 Canadian Catalysts

Effect of MMT on Catalysts
Vehicles Evaluated for Effects of MMT

Model	Miles	Type	BET(m2/g)	Mn (wt%)
Bronco II	13,545	TWC	15.5	2.62
Bronco II	13,545	COC	21.5	1.00
Bronco II	16,585	TWC	13.5	2.47
Bronco II	16,585	COC	24.4	1.36
Lynx	22,000	TWC	0.8	0.79
Lynx	22,000	COC	0.3	1.62
Tempo	22,000	TWC	7.3	4.20
Tempo	22,634	TWC	xxxx	3.13
Tempo	22,634	COC	xxxx	0.81
Topaz	24,000	TWC	13.9	1.43
Topaz	24,000	COC	7.6	0.48
Lynx	26,971	TWC	1.0	2.40
Lynx	26,971	COC	8.9	1.88
Bronco II	27,992	TWC	8.3	4.75
Bronco II	27,992	COC	4.3	2.25
Escort	28,000	TWC	4.4	1.77
Escort	28,000	COC	6.9	1.76
Topaz	28,000	TWC	14.1	3.15
Ranger	28,945	TWC	2.9	4.93
Ranger	28,945	COC	xxxx	2.48
Merkur	32,000	TWC	8.9	1.72
Merkur	32,000	COC	8.4	0.81
Escort	32,319	TWC	10.5	4.85
Escort	32,319	COC	3.4	2.87
Ranger	33,000	TWC	3.8	6.14
Ranger	33,000	COC	1.2	3.39
Aerostar	33,670	TWC	15.0	2.72
Aerostar	33,670	COC	16.4	1.57
Tempo	34,000	TWC	8.5	5.20
Escort	35,776	TWC	11.7	2.34
Escort	35,776	COC	2.7	1.98
Taurus	39,338	TWC	23.3	0.21
Taurus	39,338	COC	18.2	0.04
Bronco II	43,000	TWC	3.8	2.08
Bronco II	43,000	COC	2.7	0.83
Mustang	44,740	TWC	4.5	6.30
Mustang	44,740	COC	1.6	1.82
Tempo	47,149	TWC	2.0	4.82
Tempo	47,149	COC	0.6	2.73
Bronco II	49,467	TWC	9.0	4.89
Bronco II	49,467	COC	xxxx	xxxx

EFFECT of MMT on Catalysts

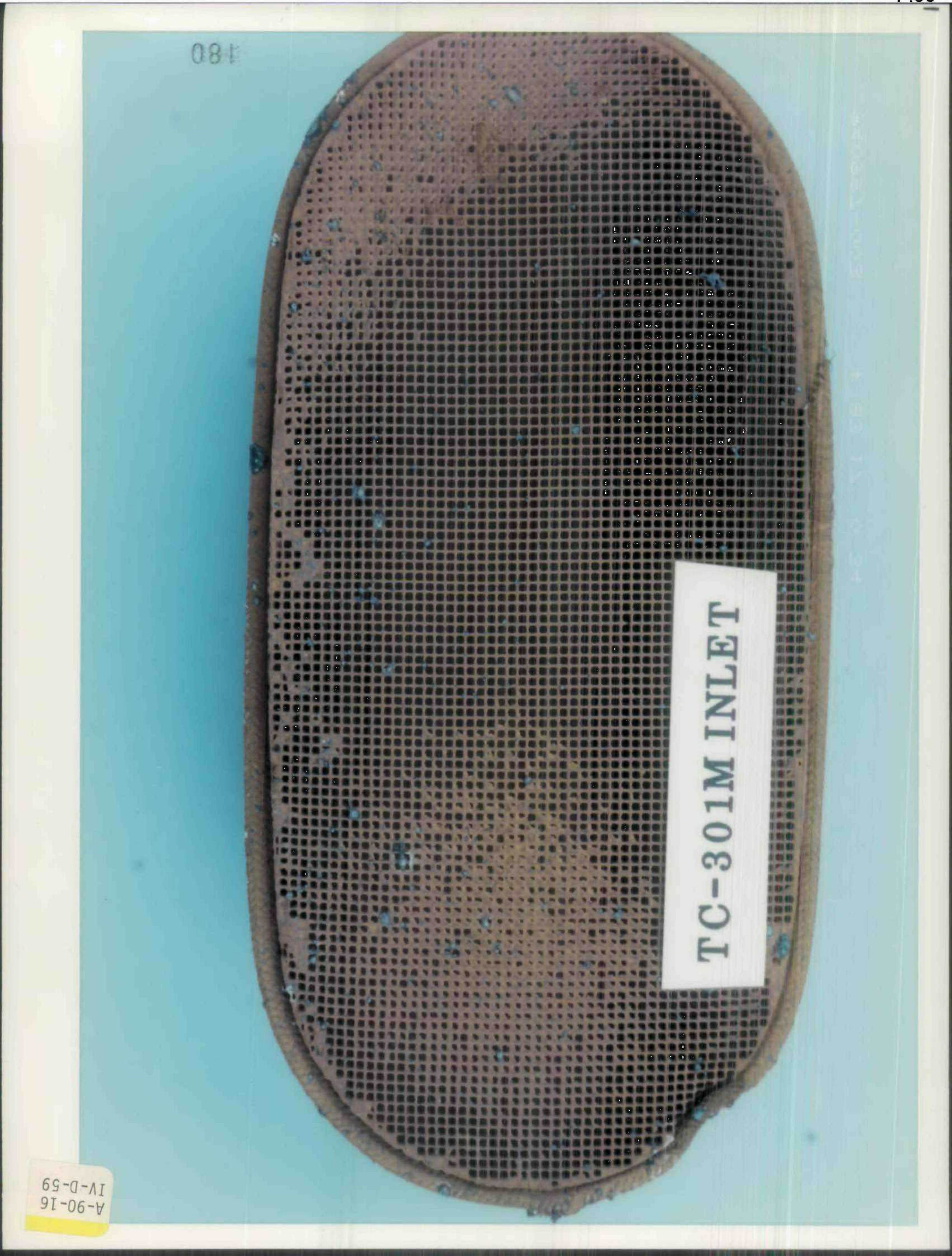
Wt% Mn	Wt% Pb	B.E.T
• 5.63	0.07	4.78
0.92		
0.60		
• 2.12	0.15	12.15
1.14		
0.87		
• 5.06	0.06	5.46
1.05		
0.82		
• 2.25	0.13	10.99
1.42		
1.13		

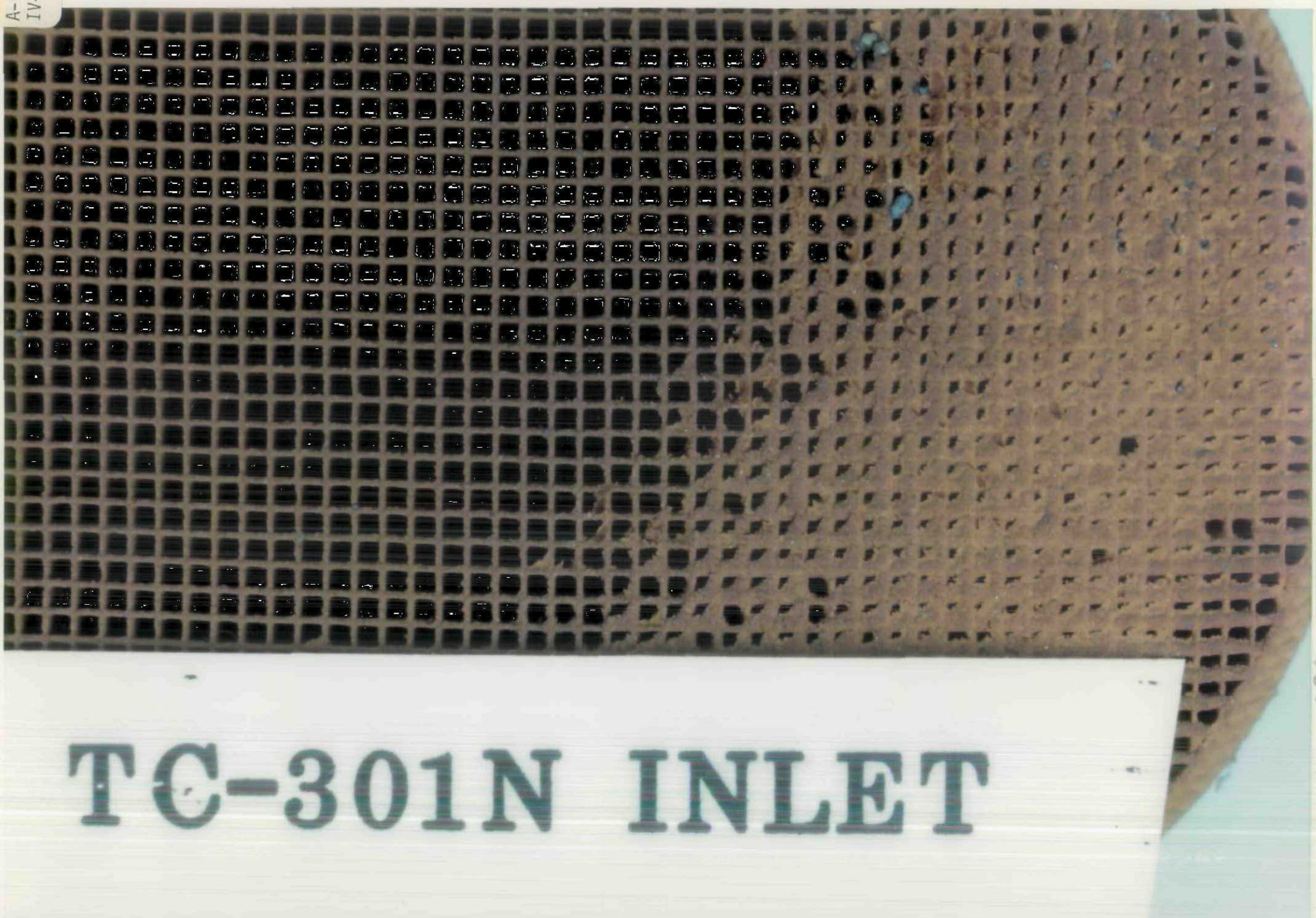
Note: Ontario Provencial Police Vehicles


08/16/88
TC 301-M
1987 5.8L LTD POLICE
ONTARIO PROVINCIAL POLICE #6245
58,121 MILES
GAS
GAS
178

A-90-16
IV-D-59

179


180
TC-301M INLET
A-90-16
IV-D-59



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